EVALUATION OF PASTE TECHNOLOGY TO CO-DISPOSE OF ASH AND BRINES AT SASOL SYNFUELS COMPLEX

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DECLARATION

I declare that this dissertation is my own, unaided work. There are, however, findings that were already reported inside SASOL that I used as part of my dissertation e.g. mineralogical data on SASOL ash, which are acknowledged in the text. It is being submitted for the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

(Signature of candidate)

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ABSTRACT

There is currently a ubiquitous drive for South African industries to improve on water usage as large volumes of raw water are consumed and saline effluents (brines) are produced during their operations. This dissertation addresses the use of paste technology to co-dispose brines as well as solid wastes, from the SASOL Secunda complex in a sustainable manner.

The findings from this study indicated that the properties of pastes with relatively high solids concentrations (e.g. 70%) are dependent on the physical properties of fly ash, such as carbon content and fineness thus impacting on the transportability of the paste. In order to overcome this effect, the paste with a 65% solids concentration will be less sensitive to the physical properties of the fly ash. Furthermore the chemical composition and salt load of brines affect the transportability and salt retention of paste. It was also observed that salinity of the brine affects the settling rate of the paste. The availability of various brines at SASOL provides an opportunity to investigate the blends of brines that will provide suitable settling and salt retention of paste. The other opportunity identified was the use of SASOL solid wastes such as incineration ash (IA) and gasification ash as additives to improve paste properties. It was also discovered that the mode of salt retention is predominantly chemical rather than physical, which increases the credibility of this technology.

The overall conclusion is that paste technology is a potential solution for sustainable co-disposal of ash and brines. Further research areas are proposed to improve the understanding of paste technology and its implementation.

DEDICATION

I would like to dedicate this work to my mother Nobelungu (MaDladla), my lovely fiancée Pamella Alam and my daughter Tumelo, not forgetting the entire Mahlaba family for their perpetual support and understanding.

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CONTENTS Page

Declaration ii

Abstract iii

Dedication iv

Acknowledgements iv

Contents v

List of Tables x

List of Figures xi

List of Plates xii

List of Abbreviations xiii

Terminology xiv

Nomenclature xvi

Chapter 1: Introduction

1.1 Introduction 1
1.2 Objectives and Research Strategy 4
1.2.1 Key issues 5
1.3 Structure of Dissertation 5

Chapter 2: The SASOL Secunda Ash System

2.1 Introduction 8
2.2 Water Recovery 10

Chapter 3: A Literature Review and Hypothesis

3.1 Introduction 13
3.2 Salts Handling 14
3.3 Fly Ash 15
3.3.1 Desired properties of fly ash 16
3.3.2 Opportunities of utilising fly ash 17
3.4 Characteristics of Ash 19
3.4.1 Chemical composition of fly ash 19
3.4.2 Physical properties of fly ash 21
3.4.3 Gasification process and ash produced 23
3.4.4 Mineralogical composition of SASOL ashes 25
3.5 Cement Chemistry 27
3.6 Brine Composition 31
3.7 Solidification/Stabilisation 32
3.8 Paste Technology 32
3.8.1 History of paste 33
3.8.2 Benefits of paste 34
3.8.3 Case studies on paste 35
3.8.3.1 Iowa power plant 35
3.8.3.2 Thickened tailings at Osborne Mine 37
3.8.4 Pumpability of Paste 38
3.9 Additives 40
3.9.1 Quick lime 40
3.9.2 Silica fume 41
3.9.3 Cement as an additive 42
3.10 Leachability Testing 43
3.10.1 Leaching tests 44

3.10.1.1 Sequential leaching 44
3.10.1.2 Toxicity Characteristic Leaching Procedure 45
3.10.1.3 Synthetic Precipitation Leaching Procedure 45
3.10.1.4 Column leaching test 46
3.10.1.5 Monolithic leaching test 46
3.11 Permeability of Paste 46

Chapter 4: Materials and Experimental Procedures

4.1 Introduction 48
4.2 Sampling of Ash 50
4.3 Brine Streams 51
4.4 Preliminary Tests of the Role of Salinity 51
4.5 Slumping Behaviour 52
4.5.1 Evaluation of a Mini-Slump Test 53
4.5.1.1 Standard cone test 54
4.5.1.2 Mini-slump test 55
4.5.2 Factors Influencing Slumping 56
4.5.2.1 LOI of fly ash 57
4.5.2.2 Fineness of fly ash 57
4.5.2.3 Time 58
4.6 Effect of Different Brines on Paste 59
4.7 Effect of Additives 60
4.7.1 Paste preparation 60
4.7.2 Remobilisation study 61
4.8 Effect of Surface Area on Remobilisation 61
4.8.1 Diffusion 62
4.8.2 Dissolution 62
4.9 Effect of Curing on Permeability 62

Chapter 5: Results and Discussion

5.1	Preliminary Test of the Role of Salinity	64
5.2	Slumping Behaviour	67
5.2.1	Evaluation of a mini-slump test	67
5.2.2	Effect of physical ash properties on slumping	68
5.2.2.1	LOI content	68
5.2.2.2	Fineness	70
5.2.2.3	Time dependence	71
5.3	Effect of Different Brines on Paste	75
5.3.1	Salts retention and slumping behaviour	75
5.3.2	The kinetics of leaching and role of eluant	78
5.4	Effect of Additives	82
5.4.1	Sieved gasification ash	82
5.4.2	Incineration ash	85
5.4.3	Lime as an Additive	86
5.4.4	Cement as an additive	88
5.4.5	Silica fume	88
5.4.6	A Comparison of different additives	91
5.5	Effect of Surface Area on Remobilisation	91
5.6	Effect of Curing on Permeability	98

Chapter 6: Conclusions and Recommendations

6.1 Summary of the Findings 100
6.2 Recommendations 103

REFERENCES 105

APPENDIX A 117

A1 The Chemical Composition of Brines 118
A2 The Role of Salinity in Bleed Behaviour 119
A3 Statistics on Slumping 121

APPENDIX B 123

B1 Conductivity Graphs on Effect of Additives 123
B2 Statistical Data Assessing the Effect of Surface Area in Leaching 127

LIST OF TABLES

Table 3.1 Typical composition of fly ash 20
Table 3.2 The percentage of phases present in GA and FA 26
Table 4.1 Materials used during the investigation 49
Table 4.2 Ratios of additive to FA 60
Table 5.1 Effect of salinity on paste behaviour 66
Table 5.2 Data on pastes prepared from various brines 76
Table 5.3 Effect of lime in permeability 87
Table 5.4 A summary of leachate analysis 97
Table A1 The chemical composition of brines 118
Table B1 Effect of SF in permeability 126

LIST OF FIGURES

Fig. 2.1 Overview of SASOL process waste handling 9
Fig. 2.2 Current understanding of salty water chain 11
Fig. 5.1 Effect of salinity in bleed formation 65
Fig. 5.2 The correlation between standard cone and mini-slump 67
Fig. 5.3 Relationship between mini-slump and LOI 69
Fig. 5.4 Relationship between increase in fineness and slumping 70
Fig. 5.5 Time dependence of slump per set of materials 74
Fig. 5.6 Relationship between initial and final TDS 77
Fig. 5.7 Conductivity plot vs time of leaching from various brines 80
Fig. 5.8 Effect of replacing eluant on remobilisation 81
Fig. 5.9 Conductivity plot versus time under various SGA additions 84
Fig. 5.10 Effect of incineration ash on salt retention 85
Fig. 5.11 Effect of lime on salt retention 86
Fig. 5.12 Effect of cement on salt retention 88
Fig. 5.13 The increase in liquid mass against SF additions 89
Fig. 5.14 Effect of SF on salt retention 90
Fig. 5.15 Testing surface area against curing time 92
Fig. 5.16 Conductivity as a function of time on remobilisation 95
Fig. 5.17 Plot of TDS as a function of time 96
Fig. 5.18 Permeability as a function of curing time 98
Fig. A2.1 Bleed behaviour of fly ash with distilled water 119
Fig. A2.2 Bleed behaviour of fly ash with U66 brine 120
Fig. A3.1 Graph showing the relationship between two slump tests 121
Fig. A3.2 The relationship between slump and LOI 122
Fig. B1.1 Conductivity trend on pastes with IA 123
Fig. B1.2 Conductivity trend on pastes with lime 124
Fig. B1.3 Conductivity trend on pastes with cement 125
Fig. B1.4 Conductivity trend on pastes with silica fume 126

LIST OF PLATES

Plate 3.1 Typical morphology of fly ash 22
Plate 3.2 Micrograph of SASOL fly ash 23
Plate 3.3 Micrograph of SASOL gasification ash 24
Plate 4.1 Set-up used to monitor settling and dehydration 52
Plate 4.2 Pictures of slump test apparatus 53
Plate 4.3 Standard cone test in action 55
Plate 4.4 Mini-slump test in action 56
Plate 4.5 Apparatus for paste preparation 58
Plate 4.6 Apparatus to determine permeability 63
Plate 5.1 Deminishing cracks per increased SGA additions 82

LIST OF ABBREVIATIONS

EC: Electrical Conductivity
FA: Fly ash
FAM: Fine Ash Make-up Water
GA: Gasification ash
IA: Incineration ash
LOI: Loss on ignition
OPC: Ordinary Portland Cement
P:E: It refers to the mass ratio of paste to the eluant
PSD: Particle Size Distribution
S:L : It refers to the mass ratio of solids to liquid in a mixture
SF: Silica fume
SGA: Sieved Gasification ash
sWA: sieved weathered ash
TCLP: Toxicity Characteristic Leaching Procedure
TDS: Total Dissolved Solids
TRO: Tubular Reverse Osmosis

TERMINOLOGY

Bleed: Is the small volume of water that forms on top of paste when solid material settles.

Brine: Is a salinated inorganic stream that requires treatment before disposal, which is a by-product effluent.

CAE: clear ash effluent refers to the recycled water used to transport ash from where it is produced into the ash system.

Electrical Conductivity: refers to the ability of a solution to carry electrical current, influenced by the number and type of ions present.

FAM: is a stream which mainly consists of recycled clear ash effluent and salty streams from different processes.

Fineness: It refers to the availability of particles of diameter less 45 μm in fly ash that provide lubrication effect due to their spherical nature.

Fly ash: refers to fresh fly ash which is a coal combustion by-product from the boilers collected from electrostatic precipitators in steam plants.

Immobilisation/Retention: It refers to the extent in which dissolved ions are either physically or chemically bound in paste such that they are less soluble when exposed to water.

Leachability: This refers to the amount of salts that will be removed (remobilised) from paste when exposed to water.

Loss on ignition (LOI): it refers to a mass percentage that is lost when a solid material e.g. ash is exposed to high temperatures.

Paste: refers to a material made from ash and water or brine that is thick, which will not significantly segregate and can harden as concrete when disposed.

Permeability: It is the resistance of a material like paste to water percolation which is often measured in cm/s.

Pozzolan: is a compound that favours the occurrence of pozzolanic reactions.

Pozzolanic/hydration reactions: This refers to a hydration process of cement or ash that results in a formation of mainly calcium silicate and aluminate hydrates.

Pumpability/transportability: refers to the ease with which paste can be transported through pumping.

Remmobilisation: refers to the test where paste is exposed to a liquid medium to assess its leachability or salt retention.

Slumping: It is a quick test that is used to determine transportability of paste to a disposal area.

Total Dissolved Solids: is a measure of the quantity of various inorganic salts dissolved in water.

NOMENCLATURE

EC	Electric Conductivity	mS/cm
k	Permeability	cm/s
TDS	Total Dissolved Solids	mg/l

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

SASOL Synfuels (Pty) Ltd in Secunda, South Africa is recognised internationally for its unique conversion of coal to liquid fuels and chemicals. SASOL produces approximately 41% of South Africa's liquid fuel through gasification of low grade coal into synthesis gas, which is a starting material for the Fischer-Tropsch process (van Dyk *et al.*, 2006). Chemicals such as surfactants, solvents and polymers are also produced.

At SASOL large volumes of water are utilised for steam generation and process cooling. The scarce nature of water, however, necessitates the recovery of water for reuse in the factory. SASOL currently desalinates some mine water using an Electrodialysis Reversal (EDR) process.

The Clear Ash Effluent (CAE) is a liquid which results from the transportation of ash slurry to the fine ash dams. CAE is then

recovered using Tubular Reverse Osmosis (TRO) to ensure zero liquid effluent discharge. However it is not sustainable to continuously desalinate water because of consequential salt loads that will concentrate the ash carrier medium. The high salt loads in the TRO feed also have a negative impact on membranes and will be detrimental to pipes due to increased risks of corrosion and scaling. It is therefore crucial that the brine streams are disposed of in a safe manner such that zero effluent discharge concept may be sustained.

Concurrently there are approximately 1200 ton/h of ash being produced as by-product. The ash is produced at high rates with approximately 200 and 700 ton/h, of fine gasification ash (≤ 250 μm) and coarse gasification ash respectively. Fly ash is produced at an average rate of 300 ton/h (Koch, 2002). The combination of fine gasification ash and fly ash constitute fine ash in the SASOL environment.

The total salts accumulating in the complex are a combination of chemicals used, raw water, mine water and salts originating from coal and ash. These salts enter the Synfuels complex at a rate of approximately 250 ton/day, and end-up in water that circulates the complex (Jeevaratnam and Pretorius, 2003). The

desalination process yields reduced volumes of highly concentrated brine streams which need to sustainably be disposed of. The resultant brine from the EDR process is handled in an expensive evaporator-crystalliser unit. There are other brine streams originating from sulphur plant, Benfield process and many other processes that will require safe disposal.

The current practice is to dispose of these salts into the ash system and solar ponds (Jeevaratnam and Pretorius, 2003; Kwak *et al.*, 2005). However ash disposal is considered an environmental risk due to its potential of underground water pollution by heavy metals and salts (Joshi *et al.*, 1993; Bin-Shafique *et al.*, 2002).

The leaching mechanism of trace elements from ash is similar to that from soil and other types of solid wastes (Koch, 2002). It is also known that fly ash has pozzolanic properties i.e. will cement in the presence of water and an activator such as lime, due to its siliceous and aluminous content (Bin-Shafique *et al.*, 2002; Joshi *et al.*, 1993; Tishmack *et al.*, 2001). An idea of exploiting the pozzolanic properties of fly ash to make a paste was generated (Jewell *et al.*, 2002).

Paste can be defined as a material that does not segregate and consists of between 75% and 85% solids by weight of which approximately 15% < 20 μm (Yilmaz *et al.*, 2004; Newman, 2003; Kwak *et al.*, 2005).

This dissertation investigates the application of paste technology as a plausible option for the disposal of brines (salts) in ash paste. There are, however, factors that require thorough investigation, to mitigate the environmental impact.

1.2 OBJECTIVES AND RESEARCH STRATEGY

The project is aimed at obtaining a sustainable solution for the disposal of brines in ash paste. Therefore, the desired product/paste should be easily pumpable, and have relatively low permeability and salt leaching.

The research strategy was to develop a relationship between the following process variables:

(a) solids concentration

(b) brine composition

(c) curing time

(d) paste stiffness and its dependence on time

(e) effect of additives

(f) effect of surface area

The effect of the abovementioned parameters was assessed by monitoring salt retention, permeability and slumping of the resultant paste.

1.2.1 Key Issues

The main challenges which were encountered during the study are summarised below.

- Pumpability of paste to the disposal area.
- The appropriate remobilisation test
- The mechanism of salt immobilisation
- The technical feasibility of either surface disposal or underground backfill.

1.3 STRUCTURE OF THE DISSERTATION

Chapter 1

SASOL is introduced as a company and its operations. The use of raw materials is discussed as well as the resultant wastes. The problem statement is also introduced for this investigation.

Chapter 2

This chapter outlines the production at the SASOL Synfuels plant in Secunda. The process is discussed with the emphasis on wastes that are generated, and the current disposal mechanisms.

Chapter 3

The general problem of industrial salts is introduced. The legal requirements and the drive for the reuse of brines and effluents are presented. Different methods exist to handle salts but paste seems to be a more suitable disposal option than the conventional slurry or tailings disposal. Some of the paste benefits include low permeability, possibility to combine solidification and stabilisation. Paste does not segregate hence there is no further water management required after placement.

Chapter 4

The starting materials and their origin are briefly described in this chapter. The different experiments and tests performed are also described.

Chapter 5

The important observations made during the study are discussed. The results are interpreted based on the available data and the areas that need further research are highlighted.

Chapter 6

A summary of important findings is given. The areas that require further research are recommended.

CHAPTER 2

THE SASOL SECUNDA ASH SYSTEM

2.1 INTRODUCTION

At SASOL Synfuels low grade coal is gasified and converted into liquid fuels and a wide range of chemicals. Two major types of ash are produced from the process namely coarse ash and fine ash (described in chapter 1). The former is produced from the gasification process while the latter mainly comes from a steam generation process (see **Fig. 2.1**).

The two ash types are processed and separated at the inside ash handling plant. However, the current approach is to dispose of most of the salty streams and brines into the ash system by introducing them at the inside ash plant. They include the spent catalyst from Synthol plant, blow-down from process cooling water systems, salty water from desalination plants and sludge from flocculation processes.

The SASOL ash and effluent handling process is summarised in **Fig. 2.1**.

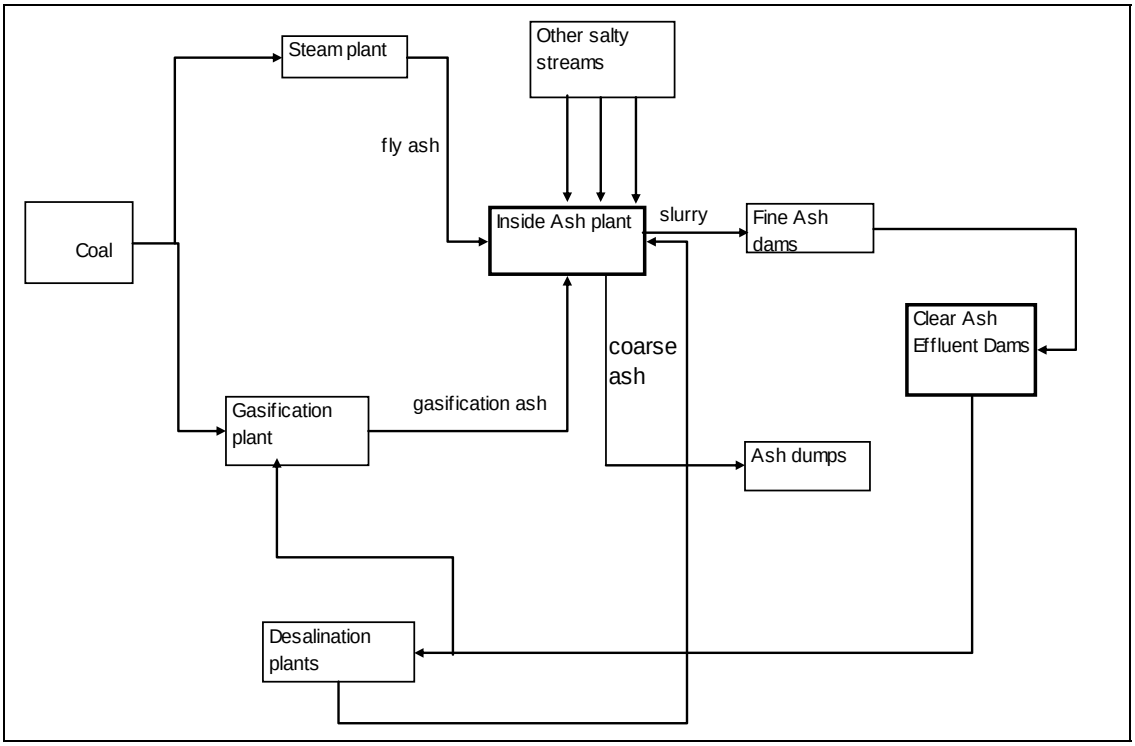

Fig. 2.1 Overview of SASOL process waste handling

The ashes therefore interact with different kinds of salts before disposal. The question of how sustainable and/or reliable this practice is has not been thoroughly addressed. Coarse ash is then transported to the ash heaps by means of conveyor belts while fine ash is transported as slurry to the fine ash dams.

2.2 WATER RECOVERY

The geographical location of Synfuels complex imposes a high risk of water pollution since it is built on the water divide of the Vaal and Olifants rivers. It was therefore essential to operate on a zero-effluent discharge concept (Basson *et al.*, 2004). This meant that no effluent discharges are allowed to the nearby rivers.

Different uses of water at the Synfuels complex generate inorganic salty effluents. Processes such as TRO and EDR are employed to recover water for further uses. The drawback of these processes is the highly concentrated brine streams which they produce. The consequence is a deteriorating water quality circulating the complex; hence these brines need to be disposed of.

CAE dams serve as temporary storage for certain brines before returning to the complex for further recovery. The implications are that salts could be accumulating and are likely to redissolve and cause environmental harm. This could happen at low pH or highly alkaline conditions (Bin-Shafique *et al.*, 2002; Klemm, 1998; Asavapisit and Cosanavit, 2004). Underground water pollution and soil

contamination are other concerns against storage of salty waters in addition to potential overflows during heavy rains (Verburg, 2001; Jewell *et al.*, 2002; Kwak *et al.*, 2005). The figure below shows the current understanding of the fate of salts.

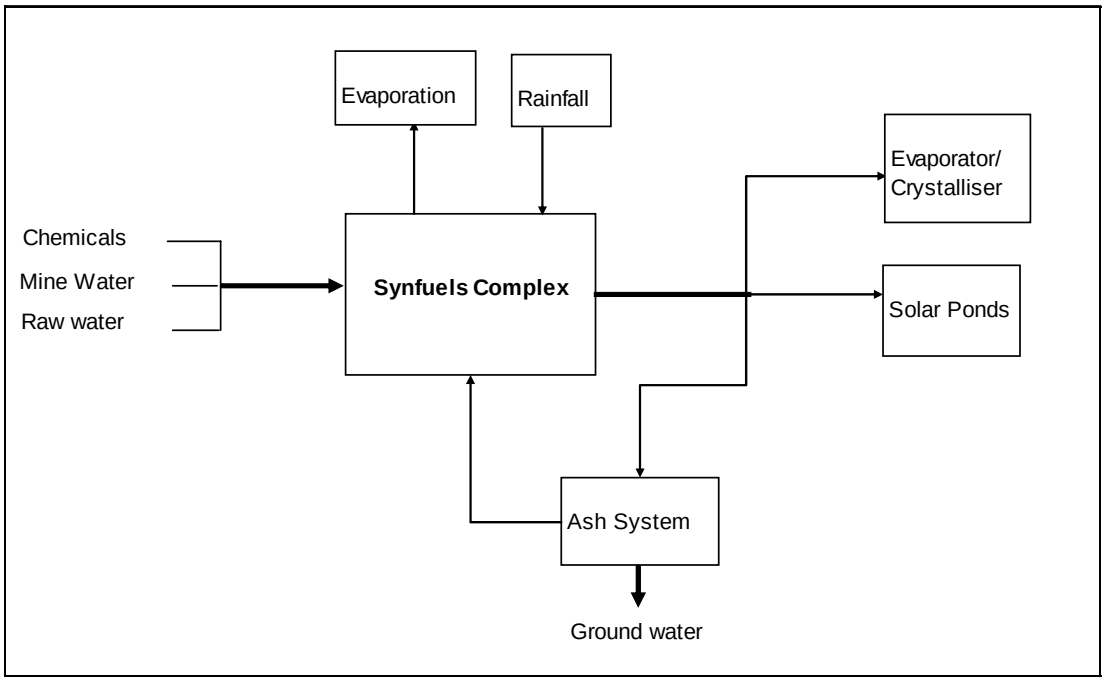

Fig. 2.2 Current understanding of salty water chain

The evaporator-crystalliser unit addresses approximately 20% of salts but is expensive and has limitations in terms of operation. On the other hand solar ponds handle approximately 35% of the salts while the rest is accounted for by the ash system. The solar ponds are nearing their capacity of salts disposal (Basson *et al.*, 2004; Ginster,

1999). The implications are that the ash system will handle more salt loads than it does at present. There are process expansions which are envisaged for the near future which will increase the salt load by approximately 15% without producing ash.

A need was identified to optimise the use of ash to immobilise salts. Research has revealed that paste renders better technical and environmental benefits over slurry (Jewell *et al.*, 2002; Joshi *et al.*, 1993; Benzaazoua *et al.*, 2003; Kaneko *et al.*, 2001). Exploration of paste technology could lead to a sustainable salt disposal.

The above-mentioned points initiated a necessity for a literature review on the disposal of salts. The literature survey would provide the necessary guidance and direction to effectively address the salts problem at SASOL Synfuels.

CHAPTER 3

A LITERATURE REVIEW AND HYPOTHESIS

3.1 INTRODUCTION

Studies have shown that water has become a scarce resource over the past few years in South Africa and other parts of the world (Haldenwang, 2005). The water demands are expected to increase in the near future due to a variety of reasons such as population and economic growth, climate changes and improved standards of living (Haldenwang, 2005). The legislative requirements are becoming more stringent towards raw water intake hence there is a huge drive towards minimal water consumption, and reuse of industrial effluents and brines (Gordon, 2001; McPhail *et al.*, 2004; Glater and Cohen, 2003; Lynch *et al.*, 2005). Most importantly, water availability and quality are both environmental and economic threats (Gordon, 2001; Glater and Cohen, 2003; Yilmaz *et al.*, 2004; Haldenwang, 2005).

3.2 SALTS HANDLING

A common approach to the handling of salts is to employ desalination technologies which produce brines as inevitable by-products (Gordon, 2001; Glater and Cohen, 2003; Walton *et al.*, 1999; Lynch *et al.*, 2005). However, handling and disposal of brines are technically challenging and costly (Verburg, 2001; Lynch *et al.*, 2005; Mahlaba and Pretorius, 2006). Salt disposal is mainly perceived as a problem for inland industries (Khordagui, 1997; Glater and Cohen, 2003; Ilgner, 2002). Coastal industries conventionally dispose of their salts into the sea using pipelines (Gordon, 2001; Khordagui, 1997; Glater and Cohen, 2003). Discharge of brines into the sea causes a change in its temperature and salinity (Fouda *et al.*, 1999) hence it is not encouraged. Small volumes of brine may easily be diluted by the sea while large volumes may have detrimental effects on aquatic life (Gordon, 2001; Glater and Cohen, 2003).

Power stations and petrochemical plants are examples of inland coal processing industries in South Africa (van Dyk *et al.*, 2005). SASOL Synfuels uses coal as a starting material to produce its wide range of products. Various salty streams and grades of ash are produced, and sustainable disposal is required

(Al-Handhaly *et al.*, 2003; Raghavendra *et al.*, 2002). The details on salty streams were given in chapter 2.

3.3 FLY ASH

The fly ash can generally be defined as a very fine by-product from a coal fired power station (Joshi *et al.*, 1999; Raghavendra *et al.*, 2002). Typical fly ash characteristics/specifications are given in section 3.4.1. A considerable amount of work has been reported on basic fly ash composition in addition to its physical and chemical behaviour (Chindaprasirt *et al.*, 2005; Lam *et al.*, 2000; Vilches *et al.*, 2005). The intention was to extend its applications beyond cement industry to include stabilisation of salts containing effluents (Ilgner, 2002; Raghavendra *et al.*, 2002). Because of both physical (particle size distribution) and chemical (pozzolanic) properties of fly ash it was decided to investigate its potential to make a paste and retain salts from the salty streams (Asavapisit and Cosanavit, 2004; Bergeson *et al.*, 1988; Chindaprasirt *et al.*, 2005).

3.3.1 Desirable Properties of Fly Ash

The fineness (defined as the mass percent of particles that can pass through a 45 μm sieve) of fly ash is a physical property that positively contribute to the pozzolanic activity and transportability of paste (Mahlaba and Pretorius, 2006; Chindaprasirt *et al.*, 2005; Ferraris *et al.*, 2001). The high pozzolanic activity is essential for the formation of desired hydration products that make paste a disposal option (Bin-Shafique *et al.*, 2002; Bergeson *et al.*, 1988; Chindaprasirt *et al.*, 2005). The presence of spherical particles in ash makes it a useful additive that increases strength and workability of cement (Ferraris *et al.*, 2001; Stropnik and Južnič, 1988; Chindaprasirt *et al.*, 2005). Pozzolanic property refers to the tendency of a material to form calcium silicate and aluminate hydrates when its glassy phase content (mainly silica, alumina and free calcium oxide) react with water (Ozyildirim, 1998; Steenari *et al.*, 1998). Further details are discussed in section 3.4.1.

3.3.2 Opportunities of Utilising Fly Ash

The utilisation of fly ash in the cement industry in India increased the durability of concrete and reduced permeability making it a potential sink for nuclear wastes (Kumar and Kaushik, 2003; Chindaprasirt *et al.*, 2005). In Italy more than 90% fly ash is used in cement and concrete industries as a legislative requirement (Belz and Caramuscio, INTERNET). The cement industry was one of the first industries to exploit the pozzolanic properties of fly ash (Griffin *et al.*, 1999).

There are many other opportunities which were identified for further fly ash utilisation in literature. They include extraction of valuable elements (e.g. aluminium), use in environmental engineering and in building materials (e.g. brick manufacturing and ceramic products) but these were limited by market constraints (Fatih *et al.*, 2001; Raghavendra *et al.*, 2002).

A closer look at the synthesis of phosphate ceramics generated a potential use of fly ash. Positive results were obtained for the utilisation of fly ash in construction by allowing it to react with phosphoric acid in the presence of magnesium oxide and boric acid (Banerjee, 1997). The major product formed was an

insoluble newberyite which is relatively light but strong, and does not leach (Banerjee, 1997). The retention of heavy metals and other wastes was found to be a combination of chemical and physical bonding.

Ultramarine blue is a useful dye in the production of paints, plastics, roofing granules, and detergents, just to mention a few (Landman and de Waal, 2004). The industrial production of ultramarine blue involves the activation of kaolin at high temperatures of approximately 700 °C to yield aluminosilicate which is a major starting reagent (Landman and de Waal, 2004). However, a potential to extract aluminosilicate from fly ash was identified and tested with an intention to discover a cheaper option and to minimise the tonnages of ash disposal (Landman and de Waal, 2004). The higher content of iron in the fly ash used limited the success of the ultramarine production to 80%. Endeavours were made to prepare zeolites and cracking catalysts from fly ash (Raghavendra, *et al.*, 2002). The outcome of the study was not discussed.

3.4 CHARACTERISTICS OF ASH

In the section above potential uses of fly ash in a variety of situations were discussed. Deeper examination of the properties of fly ash explains its versatile applications. A brief account will be made on gasification ash. The differences between the two types of ash will be covered as well as those determined at SASOL. This would allow for the identification of discrepancies or new opportunities especially with gasification ash.

3.4.1 Chemical Composition of Fly Ash

Studies on fly ash have shown that it consists of the ingredients that are essential for pozzolanic reactions to occur (Grey *et al.*, 2003; Raghavendra *et al.*, 2002; Mobasher *et al.*, 1996; Thomas *et al.*, 2001). The spherical morphology of fly ash reduces friction between the particles and improves the workability of paste or concrete (Ferraris *et al.*, 2001; Stropnik and Južnič, 1988). The elemental composition of fly ash depends on the coal source (Bin-Shafique *et al.*, 2002).

Fly ash is usually classified into two classes. Fly ash is either a class C or a class F depending on the original coal that was

burnt as well as the composition thereof (Bergeson *et al.*, 1988; Scheetz, 2004; Bin-Shafique, 2002). Class F fly ash usually has low calcium content and originates from burning of anthracite or bituminous coal (Bin-Shafique, 2002). Class C fly ash normally results from burning of lignite or subbituminous coal and exhibit self-cementing properties due to high calcium content. The mineralogy and crystallinity of fly ash depend on combustion technology and operational conditions used (Bin-Shafique *et al.*, 2002). Typical values of the constituents found in the two classes of fly ash are shown in **Table 3.1** (Scheetz, 2004; Mishra and Patel, 2004).

Table 3.1: Typical composition of fly ash (% weight)

Chemical Species	Class C	Class F
SiO_2	37	50
Al_2O_3	18	23
Fe_2O_3	6	7
CaO	25	8
MgO	5	1.5
K_2O	0.6	1.5
Na_2O	1	1
TiO_2	3	4

SO_3	3	1
Loss on ignition (LOI)	1.5	2.5

3.4.2 Physical Properties of Fly Ash

Fly ash particles range from as small as 0.01 μm to about 100 μm, with 50 μm being a typical particle size (Koch, 2002; Mashra and Patel, 2004). Particle size distribution (PSD) is one of the important parameters of ash which made it attractive in the cement industry (Kesimal *et al.*, 2003; Sear, 2001).

It is well reported in literature that fineness (defined as mass percentage in fly ash passing through a 45 μm sieve) plays a crucial role in the workability and cementing potential of pastes (Ferraris *et al.*, 2001; Chindaprasirt *et al.*, 2005). The minimum requirement for fineness is 60% in fly ash (Sear, 2001). The importance of these particles is mainly in their spherical morphology. This morphology results in reduced friction between the particles making it easier to pump with minimal water requirements (Ferraris *et al.*, 2001; Yijin *et al.*, 2004). Less water requirements result in low permeability and bleed formation, which lowers the chances of paste segregation

(Pagé and Spiratos, 2000; Bergeson *et al.*, 1988; Chindaprasirt *et al.*, 2005; Joshi *et al.*, 1999). The typical morphology of fly ash is shown in **Plate 3.1.**

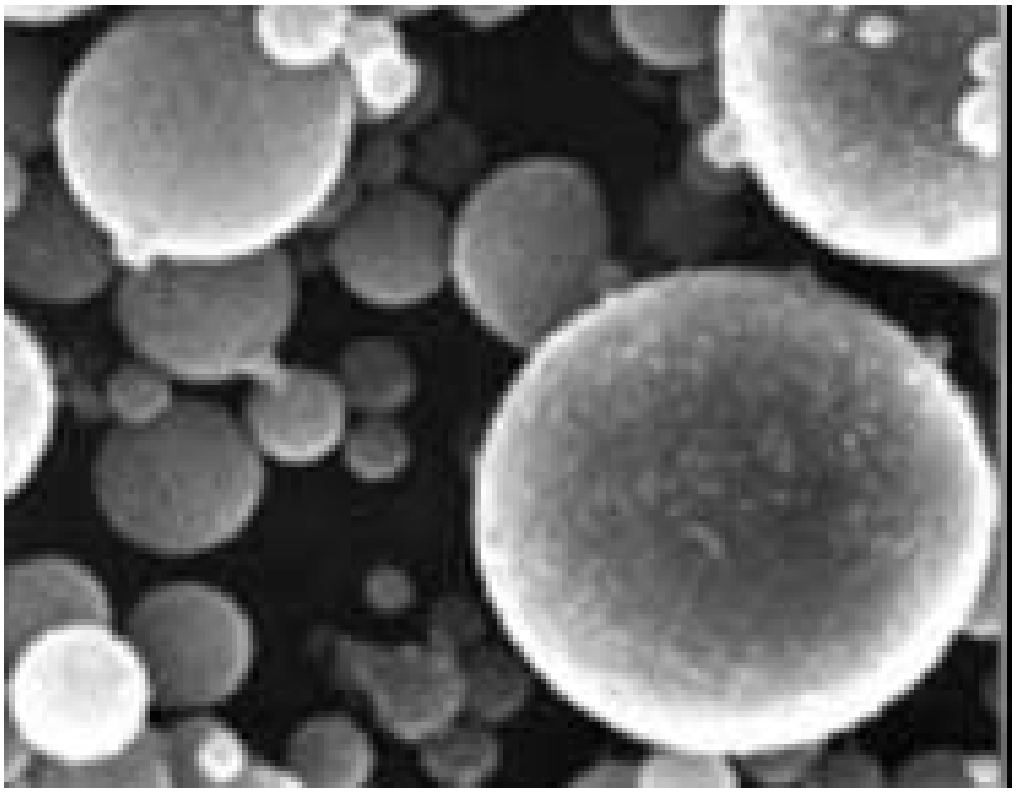

Plate 3.1: Typical morphology of FA

A sample of SASOL FA was analysed using scanning electron microscope (SEM) analysis at SASOL R&D and a micrograph is shown in **Plate 3.2**.

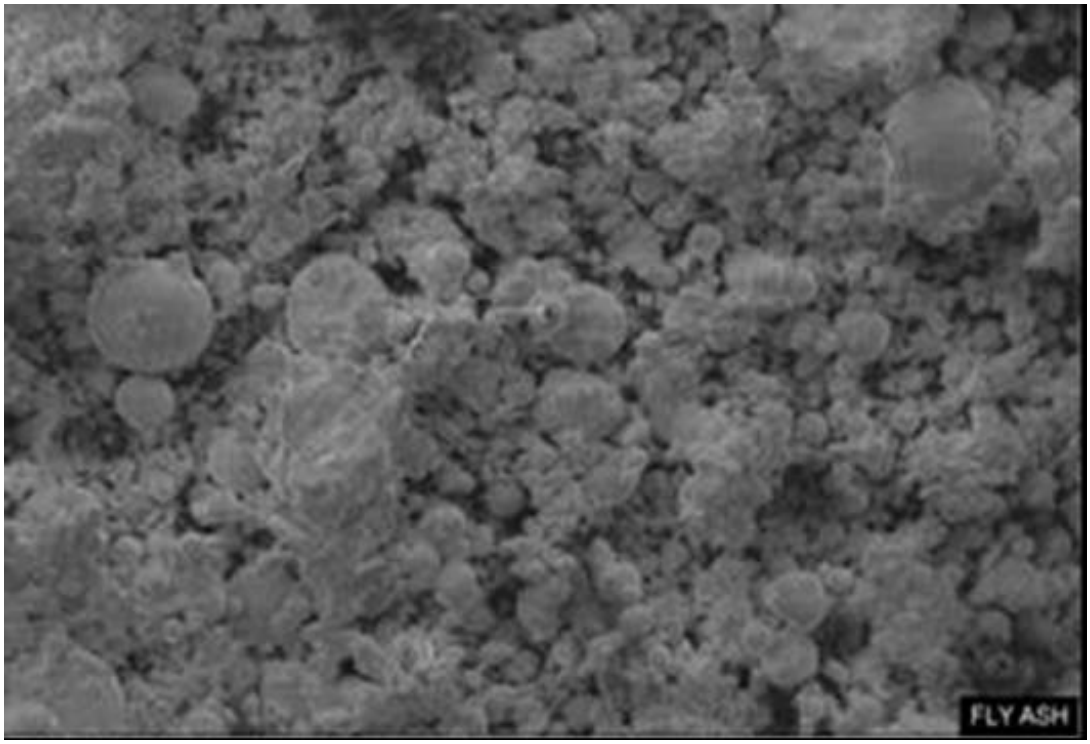

Plate 3.2: Micrograph of SASOL FA

The majority of the particles are spherical in shape although there are some particles that seem to have agglomerated into irregular particles. There also seems to be some deposits on the surface.

3.4.3 Gasification Process and Ash Produced

Coal is supplied to the SASOL-Lurgi fixed bed gasification process. Gasification can be defined as a conversion of coal through interaction with air and steam at high temperature (> 700 °C) to syngas (H_2 and CO) which can be used as a source of

energy or synthesis of chemicals and liquid fuels (Collot, 2005; van Dyk *et al.*, 2005). The advantages of gasification process include high efficiency and low emissions of NO_x and SO_2 to the atmosphere (Harris *et al.*, 2004). It was discovered in Spain that gasification ash is more suitable for element extraction than boiler fly ash (Font *et al.*, 2005). This difference was explained in terms of operating conditions such as temperature and pressure (Font *et al.*, 2005).

A sample of fine gasification ash (as described in chapter 1) was sent for SEM analysis. The picture shown below was obtained during SEM analysis at SASOL internal laboratory.

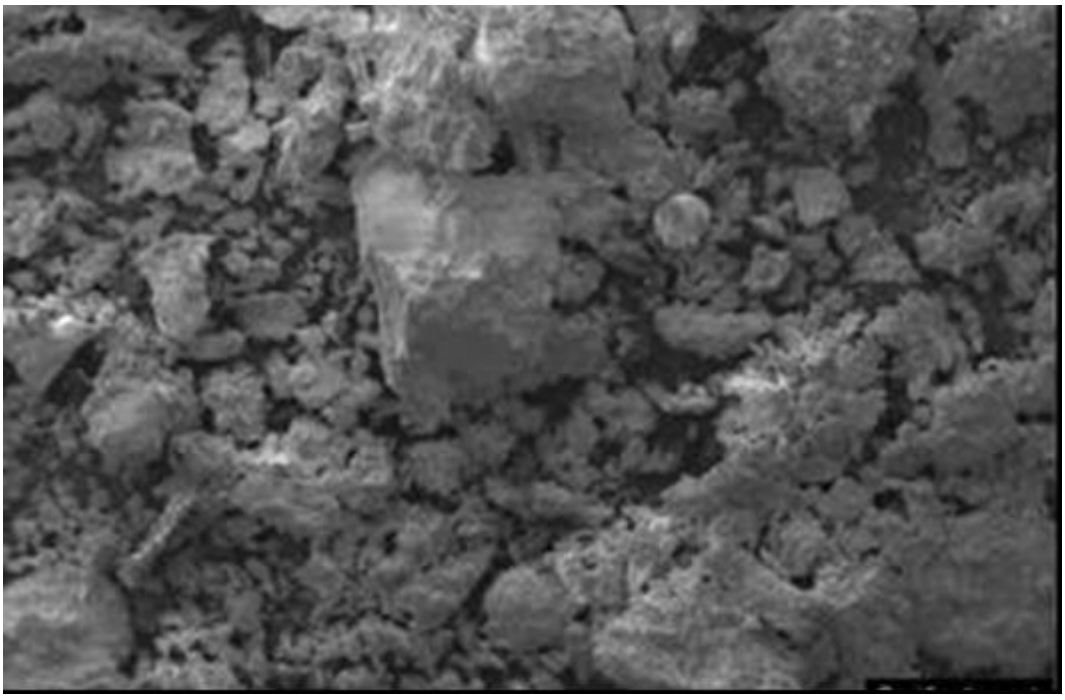

Plate 3.3: Micrograph of GA

A micrograph of gasification ash (GA) is shown in **Plate 3.3**. The particles are mainly irregular in shape, including the agglomerated particles from finer particles (Zevenhoven-Onderwater *et al.*, 2001). The morphology is quite different from that of fly ash (Font *et al.*, 2005).

3.4.4 Mineralogical Composition of SASOL Ashes

The operation conditions at the gasification plant are different from those applied at the steam plant, which is likely to cause a difference in ash produced from the two processes (Matjie *et al.*, 2004; Bin-Shafique *et al.*, 2002; Scheetz, 2004). A detailed study was conducted on both fly ash and gasification ash with an intention of obtaining mineralogical information after undergoing different processes. The samples were analysed using Coal Characterisation Scanning Electron Microscope (CCSEM) in the laboratory of Eskom TSI (Technology Services International).

Table 3.2: The percentage of phases present in GA and FA

Phase	% Fly Ash	% Gasification Ash
Interstitial/matrix (aluminio-silicate) glass with minor Ca,Mg,Fe and Ti	10.5	30.9
K-bearing glass (transformation products of microcline and muscovite)	2.5	3.2
Anorthite ($CaAl_2Si_2O_8$).	0.0	8.7
Mullite ($Al_6Si_2O_{13}$)	2.7	2.8
Quartz (SiO_2)	14.0	11.7
Aluminio-silicate (transformation products of kaolinite)	56.0	27.0
Pyrrhotite/Fe-S-O/Fe-oxide (transformation of extraneous pyrite)	1.4	3.5
CaOxide/CaMgOxide/CaFeOxide (transformation of extraneous carbonates)	4.3	1.4
Char	4.2	3.2
Other	4.5	7.5

The results obtained during characterisation indicated that gasification ash contains approximately 30% glass phase while fly ash contains at most 10% of the glass phase (Matjie *et al.*,

2004). Further details are supplied in **Table 3.2**. The implication of these differences could be important in terms of pozzolanic reactions (Tishmack *et al.*, 2001; Vilches *et al.*, 2005).

3.5 CEMENT CHEMISTRY

Fly ash is regarded as a useful pozzolan in many types of industries (Ferraris *et al.*, 2001; Ozdemir *et al.*, 2001). Furthermore the physical properties discussed in 3.4.2 positively affect the workability of concrete (Ozdemir *et al.*, 2001; Mahlaba and Pretorius, 2006). The composition of fly ash is similar to the composition of ordinary cement hence understanding of cement chemistry is crucial (Tishmack *et al.*, 2001; Sumranwanich and Tangtermsirikul, 2004; Ozdemir *et al.*, 2001).

Cement has a high content (>50%) of tricalcium silicate (C_3S = $Ca_3.SiO_5$) which undergoes hydration as follows:

$C_3S + nH_2O \rightarrow Ca(OH)_2 + C\text{-}S\text{-}H$ ……(1)

C-S-H known as calcium silicate hydrate is the main binding component in concrete which provides strength and durability (Le Bellégo *et al.*, 2000). This is a gel with the following

composition $xCaO.ySiO_2.zH_2O$, where x, y and z are the coefficients (Klemm, 1998). C-S-H can serve as a centre for chemisorption of hazardous ions although they can leach out since this is a physical phenomenon (Klemm, 1998). C-S-H is an extremely fine and amorphous material of variable composition contributing approx. 50% of hydrated cement paste. Calcium hydroxide contributes about 25% while the rest come from minerals such as ettringite (Neuwald$_2$, 2004).

Tricalcium aluminate (C_3A = $Ca_3.Al_2O_6$) is also present but in small quantities. C_3A undergoes hydration quicker than C_3S and forms C-A-H, reminiscent of equation (1).

$C_3A + nH_2O \rightarrow Ca(OH)_2 + C\text{-}A\text{-}H$ ……(2)

Reaction illustrated on equation (2) is only applicable in sulphate deficient environments.

A different product called ettringite forms in the presence of sulphate ions often represented as gypsum ($CaSO_4.2H_2O$). It is a complex mineral of hydrated calcium aluminosulphate with the chemical formula $Ca_6[Al(OH)_6]_2(SO_4)_3.xH_2O$ where x = 26 or 32 (Prasad *et al.*, 1999).

$Ca_3.Al_2O_6 + CaSO_4.2H_2O + nH_2O \rightarrow$ Ettringite ……..(3)

Formation of ettringite is often unwanted in hardened concrete because it causes expansion which leads to structural damage (Prasad *et al.*, 1999). Many researchers have conducted work on ettringite formation. It was found that early ettringite formation, which occurs immediately in fresh concrete does not result in any damage (Collepardi, 2003).

However, the formation of ettringite at a later stage i.e. in hardened concrete causes expansion and hence structural damage (Klemm, 1998; Collepardi, 2003). This is often due to a conversion of monosulphate aluminate hydrate (Ksp= 3.7×10^{-30}) into ettringite when sulphates become available (Klemm, 1998). Expansion is caused by the fact that ettringite has a bigger molecular mass than monosulphate aluminate hydrate, see equation 4 below.

$$Ca_4Al_2O_3SO_412H_2O + 2CaSO_4.2H_2O + 16H_2O \rightarrow Ca_6[Al(OH)_6]_2(SO_4)_3.32H_2O \quad \ldots\ldots\ldots (4)$$

There are, however, benefits that are associated with ettringite formation. It is a very insoluble mineral (Ksp= 2.8×10^{-45}) that can be perceived as a sink for sulphate ions, calcium ions and water molecules when looking at its chemical formula (Klemm, 1998; Tishmack *et al.*, 2001). The other environmental benefit is the potential of exchanging sulphate ions for oxyanions from

heavy metals such as boron and chromium (Klemm, 1998; Klemm and Bhatty, 2002; Tishmack *et al.*, 2001).

The presence of high chloride concentrations in water is a concern due to the risks of steel corrosion especially in the cooling water systems (Beaudoin *et al.*, 1990; Abdel-Wahab *et al.*, 2002; Sumranwanich and Tangtermsirikul, 2004; Arya *et al.*, 1989). However, chlorides can be chemically immobilised by the formation of Friedel's salt or be physically adsorbed on to C-S-H gel (Pagé and Spiratos, 2004; Justnes, 2004; Walcarius *et al.*, 2001). The formation of this salt is mainly dependent on the availability of aluminate and aluminoferrite (C_3A and C_4AF), and curing time (Sumranwanich and Tangtermsirikul, 2004). A competition exists when both sulphate and chloride ions are present for aluminate. However, sulphates bond more strongly to the aluminate than chlorides hence either ettringite or monosulphate aluminate is formed (Csizmadia *et al.*, 2000).

$$Cl^- + Ca_3.Al_2O_6 + nH_2O \rightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O \quad \cdots\cdots(5)$$

The solubility product of Friedel's salt is 1×10^{-30} making it rather insoluble. This salt is stable at high pH values (pH > 12) but will be destroyed at lower pH values (Csizmadia *et al.*, 2000). Friedel's salt has the ability to attract anions by ion exchange (Walcarius *et al.*, 2001). On the other hand, chlorides

were observed to increase the rate of lime hydration in the lime industry (Anthony *et al.*, 2003).

There are other mechanisms by which chlorides can be retained in paste, namely, formation of a complex calcium oxychloride, $C_3F.CaCl_2.H_{10}$ (i.e. $Ca_3.Fe_2O_6.CaCl_2.10H_2O$) and through bonding with C-S-H gel (Csizmadia *et al.*, 2000; Dhir and Jones, 1999). It was also found that the parent cation of the sulphate influences the chloride retention. Better chloride retention was obtained from pastes containing $CaSO_4$ than those with Na_2SO_4, for equivalent sulphate concentrations (Csizmadia *et al.*, 2000).

3.6 BRINE COMPOSITION

The major constituents of the brines at the Synfuels complex are halite (NaCl) and thernadite (Na_2SO_4) (Basson *et al.*, 2004). The sulphates can be as high as 20 000 mg/l in certain brine streams. The chlorides on the other hand range from 500 mg/l to approximately 35 000 mg/l. The concentrations of calcium, magnesium, sodium and potassium are also relatively high. The detailed chemical composition of various brine streams are given in **Table A1** on page 118.

3.7 SOLIDIFICATION/STABILISATION

Stabilisation/solidification (S/S) process is one of the recognised technologies that require pozzolans (e.g. fly ash and cement) to retain hazardous wastes both physically and chemically into a stable solid form (Li *et al.*, 2001). This technology is more suitable for radioactive wastes and those containing heavy metals (Asavapisit and Cosanavit, 2004; Wilk, 1999). The type of pollutants in SASOL brines is mainly inorganic. Furthermore, the solids to liquid (S:L) ratios are relatively higher in the stabilisation/solidification process making it unsuitable for SASOL since brines are in excess compared to ash.

3.8 PASTE TECHNOLOGY

There is a positive water balance at Synfuels because of the brines which are in excess. The storing dams and solar ponds are nearing their capacity which is an environmental concern (Billik and Mashike, 1991; Ginster, 1999; Jewell *et al.*, 2002). The disposal of ash is a lesser concern than that of brines for the reasons discussed in chapter 2. A slurry system is currently being employed at Synfuels and large volumes of leachate

(called Clear Ash Effluent) are generated and kept in the storage dams. The use of storage dams is notorious due to the negative environmental impacts associated with it (Fourie, 2002; Kwak *et al.*, 2005). Mines in most parts of the world had to revert from the practice of storing tailings in the dams due to many accidents that occurred where dams overflowed (Jewell *et al.*, 2002; Kwak *et al.*, 2005). People were often killed and the environment was polluted (Jewell *et al.*, 2002; McPhail *et al.*, 2004; Kwak *et al.*, 2005). This led to a strict legislation for tailings disposal and a reliable technology had to be developed (Benzaazoua *et al.*, 2004b).

3.8.1 History of Paste

The first attempt to thicken and dispose of tailings as paste on the surface was made in Canada in 1973. A different approach was independently evaluated in Germany around the same time, where underground disposal of thickened tailings (paste) was an objective (Jewell *et al.*, 2002).

Paste technology is normally employed to dispose of tailings through dewatering of the slurry for either surface disposal or underground backfill (Cincilla *et al.*, 1998; Stropnik and Južnič, 1988; Fourie, 2002; Kwak *et al.*, 2005). The actual ratio

of solids to liquid (S:L) will depend on the nature of the materials being used (Kwak *et al.*, 2005; Verburg, 2001). The solids concentration required for paste properties will always vary depending on the nature of both solids and liquid involved (Jewell *et al.*, 2002; Verburg, 2001).

3.8.2 Benefits of Paste

The main hydration products of paste are calcium hydroxide, C-S-H and ettringite where immobilisation of undesired ions is achieved by physical and/or chemical phenomena (Klemm *et al.*, 2002; Verburg, 2001).

Some of the advantages of paste over slurry/tailings are listed below:

- high content of solids is blended with liquid hence less bleed or leachate can be generated and require treatment
- has relatively low permeability hence better salt retention
- its preparation allows for use of additives to ameliorate beneficial properties.

Paste technology was therefore selected for further investigation and technical feasibility at SASOL. The motivation

was that suitable brines will be disposed of in ash paste and little resultant bleed will be produced (Jewell *et al.*, 2002; Fourie, 2002). The reduction in bleed implies mitigated environmental impact and less need for leachate management (Jewell *et al.*, 2002; Bergeson *et al.*, 1988).

A good quality paste is known to have low permeability and has the ability to harden as concrete (Stropnik and Južnič, 1988; Joshi *et al.*, 1993; Kaneko *et al.*, 2001; Chindaprasirt *et al.*, 2005). The reduction in permeability, and hardening could allow for the encapsulation of ions (Li *et al.*, 2001) that don't form minerals through chemical bonding e.g. sodium and potassium.

3.8.3 Case Studies on Paste

3.8.3.1 Iowa power plant

Iowa coal fired power plants in USA were faced with a problem of large tonnages of fly ash. A detailed study on Iowa fly ash was performed where both physical and chemical analyses were done with the aim of extending the applications of fly ash (Bergeson *et al.*, 1988).

Paste was one option for surface disposal of excess fly ash since a small portion was utilised in the cement industry as an additive (Bergeson *et al.*, 1988; Grey and Briggs, 2003). The study included determination of compressive strength, permeability and factors that affect paste behaviour e.g. loss on ignition (LOI).

Results showed that mode of curing (air curing or humid curing) may be important for paste stability. The mineralogy and chemistry of paste were dependent on particle size distribution (PSD) of fly ash. The contents of sodium, sulphate bearing minerals, lime and C_3A in fly ash affected the formation of hydration products. The ash pastes with high contents of monosulphoaluminate and straetlingite ($Ca_2Al[(OH)_6AlSiO_{2-3}(OH)_{4-3}]\cdot 2.5H_2O$) as hydration products showed high compressive strengths. The ash pastes composed of ettringite as the major hydration product were weaker.

There are other important results discussed in the full report by Bergeson *et al*. However, only the points relevant to this work were selected and discussed.

3.8.3.2 Thickened Tailings at Osborne Mine

Osborne Mine in Australia started operating in 1996 and was generating approximately 112 000 ton/month of tailings (McPhail *et al.*, 2004). It is a copper-gold operation that mines ironstone deposits containing pyrite (FeS), chalcopyrite ($CuFeS_2$) and magnetite (Fe_2O_3). Water is a scarce resource in this part of Australia hence there is a drive from the authorities to minimise water utilisation.

Significant amounts of water were lost through evaporation in tailings dams. This led to an investigation and implementation of a thickened tailings discharge. The presence of sulphides was a concern since it has a potential to generate acid (McPhail *et al.*, 2004; Benzaazoua *et al.*, 2002) and destabilise minerals essential for the success of this technology (Klemm, 1998; Benzaazoua *et al.*, 2004a; Benzaazoua *et al.*, 2002). Lime was added to neutralise the effect of sulphides and further tests showed that acid generating reactions are slow (McPhail *et al.*, 2004).

The implementation of thickened tailings discharge in Osborne provided both economic and environmental benefits. Reduction in operation costs and better rehabilitation potential were

realised in addition to water saving (which an economic and environmental issue) (McPhail *et al.*, 2004; Benzaazoua *et al.*, 2004b).

There were further details in the case study which were not discussed in this manuscript.

3.8.4 Pumpability of Paste

The transportability of paste is usually a major issue that affects its implementation. The conventional tailings or slurry contain low solids concentrations which require relatively low energy (Stivatstis, 2002; Benzaazoua *et al.*, 2004a). Paste transportation can only be achieved by making use of positive displacement pumps because of its thickness and high viscosity (Yilmaz *et al.*, 2004; Stivatstis, 2002; Paterson, 2001). The addition of plasticizers might be necessary at an additional cost to lower energy requirements (Mahlaba and Pretorius, 2006; Yilmaz *et al.*, 2004). In practice paste is usually pumped over a distance of 3 km (Yilmaz *et al.*, 2004). Transportation of paste was therefore evaluated as one of the factors that will determine its feasibility.

The standard cone slump test is used to get an indication of paste pumpability (Clark *et al.*, 1995). A modified dimensionless slump test was investigated and reported by Pashias, which requires less material than the former (Pashias *et al.*, 2000). This provided an attractive option to SASOL because sampling is difficult. Modified slump can also be used to determine yield stress. The results were compared with those obtained from using sophisticated vane techniques (Gawu and Fourie, 2004). It was concluded that modified slump test is a reliable and cheap prediction of yield stress (Gawu and Fourie, 2004). The yield stress is used for pump designs (Stivastis, 2002; Ferraris *et al.*, 2001).

The effect of loss on ignition (LOI) and fineness of fly ash in pumpability of paste was investigated. It is reported in literature that can affect the slumping behaviour of paste (Mahlaba and Pretorius, 2006; Bergeson *et al.*, 1988; Joshi *et al.*, 1993). Further details are provided in chapter 4.

3.9 ADDITIVES

The use of additives/pozzolans started long time ago (ca 4500 BC) by ancient Greeks and later Romans who built structures of which some are still standing today, using a combination of lime and volcanic ash (Neuwald, 2004a). Some of the additives are industrial wastes, which need to be disposed of. The investigation of their potential uses bears economic, environmental and technological benefits (Christodoulou, 2000). The general role of additives is to improve durability and binding through proper particle packing in the paste matrix (Neuwald, 2004b). They also reduce the amount of heat evolved during hydration (Pagé and Spiratos, 2000; Collepardi *et al.*, 1978; Backe *et al.*, 1999).

3.9.1 Quick Lime (CaO)

The presence of lime in Class C fly ash is responsible for the self-cementing property (Joshi *et al.*, 1994). Small additions of lime (such as 1.5%) can be used to activate pozzolanic reactions (Mobasher *et al.*, 1996). Lime is widely used in the softening process of industrial effluents and drinking water (Abdel-Wahab *et al.*, 2002). The modification of lime/soda softening into ultra-high lime treatment results in an effective

removal of scalants such as carbonate, phosphate and silica in addition to calcium and magnesium (Abdel-Wahab *et al.*, 2002). Furthermore the addition of lime to fly ash has made it possible to produce stabilised road-base in the presence of aggregates (Bin-Shafique *et al.*, 2002).

3.9.2 Silica Fume

Silica fume is a by-product from the production of silicon metal or ferrosilicon alloys containing approx. 90% SiO_2 (Neuwald, 2004b; Bagherpour and Choobbasti, 2003; Christodoulou, 2000). The particles are extremely small (ranging from 0.1 to 1 μm) and spherical in shape which increases the surface area of the material (Ferraris *et al.*, 2001; Ma and Dietz, 2002).

The hydration reactions previously showed in equations (1) and (2) yield calcium hydroxide in addition to C-S-H. Silica fume has proven to pozzolanically react with calcium hydroxide producing a finer product that reduces permeability by closing the voids in the matrix (Ma and Dietz, 2002; Neuwald, 2004a). The use of microsilica in concrete favoured the formation of C-S-H over ettringite (Bagherpour *et al.*, 2003). The addition of silica fume in concrete increased its chloride resistance (Hooton

et al., 1997). Furthermore it was observed that cement pastes containing approximately 30% silica fume was more prone to leaching than a control paste. This was probably due to a reduction in pH leading to the solubility of Friedel's salt (Beaudoin *et al.*, 1990).

3.9.3 Cement as an Additive

Cement is extensively used as a key ingredient in concrete for the construction of houses, buildings, bridges etc. The use of cement has been extended to environmental waste handling (Bin-Shafique *et al.*, 2002). Pozzolanic reactions take place when cement and fly ash are mixed in the presence of water and cementitious materials are formed with increased strength and workability (Bin-Shafique *et al.*, 2002; Joshi *et al.*, 1994).

Processes such as solidification/stabilisation (S/S) make use of cement as an additive to mitigate the environmental impact of industrial waste before land disposal (Li *et al.*, 2001). The major components of cement are tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite and gypsum (Chapman, 1971; Christodoulou, 2000). Use of cement during S/S increases the retention of inorganic compounds

(Wilk, 1999). This can be achieved through formation of insoluble compounds such as hydroxides and carbonates, as well as physical encapsulation (Wilk, 1999). Cement has also enhanced treatment of organic wastes by binding free wastewater into hydration products and reduction in permeability (Wilk, 1999; Li *et al.*, 2001).

3.10 LEACHABILITY TESTING

The concern with fly ash disposal lies with its possibility to pollute surface and groundwater with hazardous elements such as selenium, arsenic, chromium, zinc and lead (Klemm and Bhatty, 2002; Bin-Shafique *et al.*, 2002; Gupta, 2005). It is a known fact that whenever water interacts with a permeable material such as soil or ash there is a chance that some of its constituents will desorb or dissolve (Bin-Shafique *et al.*, 2002).

The heavy metals are almost evenly distributed in the coal but this change during combustion (Bin-Shafique *et al.*, 2002). The remobilisation of trace elements is related to the leachant and pH. Most trace elements are remobilised under acidic conditions while those that form oxyanions are more soluble in alkaline conditions (Kim, 2005; Font *et al.*, 2005).

Brines and saline effluents pose a huge environmental risk depending on their chemical composition and concentrations. The presence of elements such as vanadium, chromium, lead, arsenic, fluoride, chloride in water makes it toxic. Other points were discussed in section 3.2.

3.10.1 Leaching Tests

It is important to select a relevant leaching procedure to assess environmental impact. There are two categories for leaching methods namely, extraction tests and dynamic tests (Hartwil and Calovini, 1999). In dynamic tests the leachant is renewed while it is not in the case of extraction. Extraction tests are agitated if steady state conditions have to be reached quickly e.g. Toxicity Characteristic Leaching Procedure (Hartwil and Calovini, 1999). Non-agitated extraction tests give an indication of leaching kinetics.

3.10.1.1 Sequential leaching

This test exposes one sample to a series of agitated extraction tests with different leaching fluids (Kim, 2003). It is possible to associate the dissolution of ions with a mineral phase based on the leachant used (Kim, 2003).

3.10.1.2 Toxicity Characteristic Leaching Procedure (TCLP) (US EPA Method 1311)

This method is meant to assess the mobility of both organic and inorganic components present in solid or liquid wastes and compare with regulatory data (Bin-Shafique *et al.*, 2002). Solid waste samples are pulverised and sieved to a particle size less than 9 mm. The method is an agitated extraction test which uses a suitable leachant depending on the alkalinity of waste (Alforque, 1996). Either a sodium acetate buffer with a pH of 4.98 or acetic acid of pH 2.88 is used. TCLP simulates landfill co-disposal of organic waste (Wilk, 1999).

3.10.1.3 Synthetic Precipitation Leaching Procedure (SPLP)

This test is similar to TCLP the only difference is the leachant, which is acidified deionised water with a mixture of sulphuric and nitric acid to a pH of 4.2 (US EPA Method 1312). This method simulates a better environmental scenario under acid rain conditions for underground and surface waters pollution (Townsend *et al.*, 2003).

3.10.1.4 Column Leaching Tests

These tests are more suitable for assessing leaching of elements from soil-fly ash mixtures (Bin-Shafique *et al.*, 2002), from permeability and residence time point of view.

3.10.1.5 Monolithic Leaching Tests

Monilithic leaching tests are mainly employed to assess the mobility of elements from a material that exists as uniform solid (Kim, 2005). Leaching usually depends on exposed surface rather than S:L mass ratio (Kim, 2005).

3.11 PERMEABILITY OF PASTE

The paste technology is attractive due to the fact that cementatious materials are used (Kaneko *et al.*, 2001; Mehta and Monteiro, 2006). This is promoted by the occurrence of the hydration/pozzolanic reactions. The hardening process of pastes makes it possible for the physical encapsulation of wastes (Chindaprasirt *et al.*, 2005). The hydration products are very fine and hence close the voids, leading to a low water permeability (Chen *et al.*, 2004; Ma and Dietz, 2002; Mehta and Monteiro, 2006). The low water permeability will limit the

leaching from paste (Verburg, 2001; Mehta and Monteiro, 2006).

Permeability can generally be described as the ability of water under pressure to pass through a porous material (McGrath, 2000). For very porous materials permeability is high such that gravity is enough to cause the flow. However, this may not necessarily be the case with cured pastes. The addition of lime in fly ash reduced the permeability of paste by two orders of magnitude to 1 x 10^{-7} cm/s (Joshi *et al.*, 1994). It was decided to design columns that will be suitable for pastes with very low permeabilities. The main concern was that a liquid could take up to two weeks to pass through the paste under the influence of gravity, which is caused a huge delay in data generation. The steel columns with a pressure regulator were hence designed based on D'Arcy's equation (McGrath, 2000). This would allow the regulation of liquid flow by adjusting the hydrostatic pressure. More details are provided in section 4.9.

The knowledge gathered during the literature survey paved a way to the types of experiments that had to be conducted. The following chapter describes the tests which were performed.

CHAPTER 4

MATERIALS AND EXPERIMENTAL PROCEDURES

4.1 INTRODUCTION

The operation of the ash disposal system was discussed in chapter 2. Furthermore the discussions in the other two chapters indicated that there is a need to look at an alternative technology for the disposal of brines and ash. The results of a literature survey led to the investigation described in this chapter.

All solid materials were dried in an oven at 105 °C to remove any water that could be trapped by the hygroscopic nature of some of these materials. No pre-treatment was considered necessary for the liquid media hence they were used as sampled. The starting materials are summarised in **Table 4.1** below. The experiments were conducted at room temperature (approx. 22 °C).

Table 4.1 Materials used during investigation

Name	Abbreviation	Description
Fly Ash	FA	Fly ash collected from the electrostatic precipitators at steam plants (U243 & U43) before contact with water.
Incineration Ash	IA	Ash resulting from incineration of dewatered sludge.
Sieved Gasification Ash	SGA	Dry ash collected from gasifier 9 at 300 ºC. It was sieved to 200 μm before use.
Sieved Weathered Ash	SWA	Ash collected from the surface of an inactive fine ash dams exposed to atmosphere. It was sieved to $\leq$ 350 μm (Outside ash area).
Ordinary Portland Cement	OPC	Ordinary grade of commercial cement
Quick Lime	Lime	Analytical grade of CaO.
Silica Fume	SF	Silica fume with surface area of 390 $\pm$ 40 m^2/g.
Distilled Water	DH_2O	Millipore water prepared at U52 laboratory.
Fine Ash Make-up	FAM	Water that transports fine ash to and from inside ash plant.

U66 Brine	U66B	Highly salinated stream collected from U66 plant (brine evaporation).
EDR Brine	EDR	Brine from EDR treatment of MW.
TRO Brine	TRO	Brine from desalination of CAE.
Salty Dam 3	SD3	Salty effluent from evaporation process.
Sulfolin liquor	SLF	Brine from sulphur plant.
Potassium carbonate stream	BEN	Potassium carbonate brine from Benfield process.

4.2 SAMPLING OF ASH

Fly ash samples were collected from all the boilers at Synfuels complex. Equivalent masses were added and mixed to make a batch sample. This was used as a starting material for all experiments. The gasification plant was built such that gasification ash is discharged to the sluiceways where it contacts water. However there is only one gasifier which allows for the collection of dry gasification ash.

4.3 BRINE STREAMS

There are a number of brine streams from various processes in the complex. The streams of various compositions selected for the study included by-products from desalination processes, namely EDR and TRO brines, U66 brine and salty dam 3 effluent (SD3) which originate from the evaporation process. Sulfolin liquor (SLF) is a by-product of sulphur plant while Benfield (from Benfield process) is a potassium carbonate stream which is high in vanadium concentration. Fine ash transport water (FAM) was included in the study. Detailed chemical composition is tabulated in the Appendix. The varied brine streams would investigate whether paste technology is affected by brine chemistry or salt load.

4.4 PRELIMINARY TESTING OF THE ROLE OF SALINITY

Approximately 20 g of FA was poured into 100 ml beakers and made into solutions containing solids concentrations ranging from approx. 55% to approx. 75%. This range is generally found to provide a non-segregating mixture (Jewell *et al.*, 2002). DH_2O and U66 brine were used as liquid media. These were thoroughly mixed and monitored visually. This made it possible

to define a range of solids concentrations in which fly ash and liquid medium could be described as a paste. Settling and bleed absorption rates were determined on mixtures from both liquid media. Mixtures of lower and upper limits in terms of S:L ratio were studied in test tubes as shown in **Plate 4.1** below.

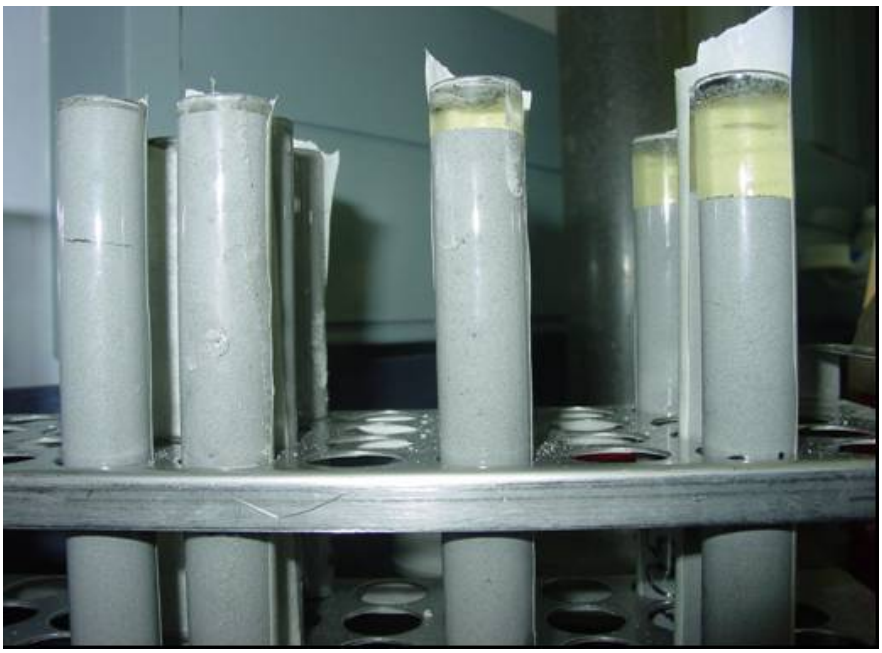

Plate 4.1 Set-up used to monitor settling and dehydration

4.5 SLUMPING BEHAVIOUR

It is common to use standard cone test to estimate the transportability of paste by measuring the slump (Yilmaz *et al.*, 2004). Novel work was reported by Pashias *et al.*, 2000 on the use of modified slump test which requires smaller volumes of sample. The possibility of a reduction in sample sizes was of particular interest in this work because; the sampling of enough

fly ash is difficult due to the infrastructure. Pashias also demonstrated that modified slump test can be used to further determine yield stress instead of sophisticated and costly vane techniques (Pashias *et al.*, 2000; Gawu and Fourie, 2004). The dimensionless slump height (ś) is expressed as (s/H); where s is the slump and H is the height of the cylinder (Clark *et al.*, 1995). The closer ś is to 1 the less energy is required to pump the paste and vice versa.

4.5.1 Evaluation of a Mini-Slump Test

The plate below shows the pictures of a standard cone (left hand side) and an open-ended cylinder (used for mini-slump on the right hand side) of the plate.

Plate 4.2 Pictures of slump test apparatus

The former requires about 7 kg of material while the latter can do with only 1 kg. The author found it necessary to evaluate the validity of using a modified slump instead of a standard cone test in this case study. The modified slump is called a mini-slump test.

4.5.1.1 Standard cone slump test

Several samples containing ca 7 kg of dried fly ash, were weighed into a mixing container, followed by a relevant mass of U66 brine or potable water to constitute the desired mass percentage concentration. A steel rod was used to thoroughly mix the contents before quantitatively transferring them to a cone. Once the cone was filled with paste, it was removed and the distance travelled by paste was measured using a ruler from the height of the cone to the centre of slumped paste. The dimensions of a cone used were; a height of 30 cm and a base diameter of 20 cm. **Plate 4.3** below shows the picture which was taken when this test was performed.

Plate 4.3 Standard slump test in action

4.5.1.2 Mini-slump test

The test was conducted in a similar manner as before except for the amount of fly ash which was reduced to 2 kg for duplicates. An open-ended PVC cylinder with an aspect ratio (Height/Diameter) of 1.2 was used to conduct the mini-slump tests instead of a cone. The test is shown on **plate 4.4** below.

Plate 4.4 Mini-slump test in action

4.5.2 Factors Influencing Slumping

It is well reported in literature that fineness (defined as % mass < 45 μm) plays a crucial role in the workability of pastes (Ferraris *et al.*, 2001; Collins and Stanley, 2003; Mehta and Monteiro, 2006). The use of fly ash as a cement replacement is limited by increases in its carbon content according to **ASTM C618**. The disadvantages include poor air entrainment, increase in water requirements, and segregation of mix components (Soong, *et al.*, 2002). The amount of carbon is quantified by a parameter known as loss on ignition (LOI). LOI was determined on fly ash samples from different boilers according to Heiri *et*

al., 2000. It was therefore decided to include the effect of these parameters in this case study.

4.5.2.1 LOI in fly ash

A series of known masses of fly ash (approx. 20 g) from different boilers were placed into pre-weighed crucibles. The samples from each boiler were exposed to 600 °C and 900 °C in a muffle furnace for five hours. The crucibles were cooled in a desiccator before weighing, and LOI was determined. The varied temperatures would investigate which component contributed to the LOI in the fly ash samples.

4.5.2.2 Fineness of fly ash

The samples from nine different boilers at SASOL Synfuels east were analysed for particle size distribution (PSD) at Synfuels laboratory in Secunda. The apparatus used was Leeds & Northrup SRA-150 Microtrac Particle Size Analyser operating in a range of 0.972 to 704 μm. The abundance of particles $\leq$ 45 μm was compared with LOI and slumping behaviour of pastes containing 65% and 70% solids concentrations.

4.5.2.3 Time

A batch sample of paste was prepared by mixing approx. 4.4 kg fly ash with approx. 9.5 kg U66 brine (according to the findings in section 4.4). A paddle mixer with a 25 litre capacity was used for paste preparation (see **Plate 4.5**).

Plate 4.5 Apparatus used for paste preparation

Triplicates of mini-slump test were performed immediately after paste preparation and thereafter at predetermined intervals shown in **Fig. 5.5**. The paste was thoroughly remixed before each mini-slump test. The paste was discarded after each slump test while paste remaining in the bowl was thoroughly sealed to eliminate the influence of air drying. The exercise was repeated

using distilled water (DH_2O) instead of U66 brine. An additional test was conducted where weathered fine ash was sieved to simulate the PSD of fly ash. A paste was made by adding U66 brine, and DH_2O to sieved weathered ash.

4.6 EFFECT OF DIFFERENT BRINES ON PASTE

The optimum S:L ratio was determined for each brine stream and fly ash as described in section **4.4**. The paste samples were prepared in duplicates and curing period was four weeks. Remobilisation study was then conducted as described in section **4.7.2**. The leachates were analysed at Synfuels laboratory for chemical composition. Metals present in leachates were determined using Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES). The chlorides were determined using Titrino while sulphates were determined using Autoanalyser. Alkalinity was titrametrically determined.

4.7 EFFECT OF ADDITIVES

4.7.1 Paste Preparation

The FA and additives were dried in an oven at 105 ºC for two hours. This was done to remove any water should these species be hygroscopic. FA and additives were individually mixed while dry according to specifications on **Table 4.2** before a liquid medium (FAM) was introduced. The numbers in **Table 4.2** represent the mass percentage of an additive which was added to FA, making a total of 68% solids contribution to the paste preparation. The dry components were thoroughly mixed for homogeneity. 32% FAM was added to the mixed components to make paste replicates.

Table 4.2 Ratios of additive to FA

SGA (%)	IA (%)	Lime (%)	OPC (%)	SF (%)
0	0	0	0	0
5	2.5	0.5	0.5	0.5
10	5	1	1	1
17	10	2	2	2
25	15	5	5	5

The ratio of 68% solids to 32% liquid was predetermined in section **4.6**. The paste samples were transferred into

polystyrene cups (250 ml) which were used as moulds, from which samples were removed after two days to facilitate air drying.

4.7.2 Remobilisation Study

The samples were weighed after four weeks of atmospheric curing before conducting remobilisation study with DH_2O. The P:E ratio (where P refers to cured paste and L to the eluant i.e. leachant solution) during remobilisation was 1:5.

Evaporation was minimised by keeping the leaching vessels closed. Conductivity and pH were regularly recorded until equilibrium was established. Leachates were filtered through GF/A filter papers and TDSs were determined. The comparison between additives was made based on conductivity and TDS values in addition to physical nature of paste in water.

4.8 EFFECT OF SURFACE AREA ON REMOBILISATION

The effect of surface area of paste in contact with water during the remobilisation was investigated. A series of paste samples were prepared using 68% fly ash and U66 brine. Polystyrene

cups were used as moulds. The effect of surface area was investigated as a function of curing time, namely 2 weeks, 5 weeks, 8 weeks and 11 weeks. The curing times were arbitrarily chosen. A set of triplicates prepared for 68% U66 brine and fly ash were also tested. These were 6.5 months old.

4.8.1 Diffusion

The intact paste samples were immersed in DH_2O, and this test was termed diffusion. The intact paste represented a scenario with a small surface area of paste exposed to water (P.E = 1:5).

4.8.2 Dissolution

The paste samples were pulverised and sieved to $\leq$ 500 µm before immersing in DH_2O. This represented a scenario where a large surface area of paste was exposed in water (P.E = 1:5).

4.9 EFFECT OF CURING ON PERMEABILITY OF PASTE

The apparatus showed on **Plate 4.6** below was used to determine permeability in cured pastes. Permeability constants were calculated according to D'Arcy's equation: $\mathbf{k = (Qx\ell)/(Axh)}$ where **Q** = flow rate of the leachate (cm^3/s), $\boldsymbol{\ell}$ =

thickness of cured paste (cm), **A** = cross-sectional area (cm^2) while **h** = applied pressure (cm) (McGrath, 2000).

Plate 4.6 Apparatus to determine permeability

Approximately 1 kg ash was mixed with U66 brine to make a paste consisting of 68% solids concentration. The contents were thoroughly mixed and quantitatively transferred into the steel columns open to atmosphere. The samples were cured up to 27 days and permeability was determined at different curing times. This would investigate the role that curing plays in permeability of a paste

CHAPTER 5

RESULTS AND DISCUSSION

5.1 PRELIMINARY EVALUATION OF THE ROLE OF SALINITY IN PASTE

A pumpable paste was found in the range of 65% to 70% solids (fly ash) with U66 brine while it was found between 67% and 73% solids with DH_2O. The two ranges are very similar and they even overlap between 65 and 70%. However it was observed that the amounts of bleed (expressed as the percentage of the total mixture) formed were extremely different (see **Fig. 5.1**). The paste prepared using a less saline medium formed more bleed. The bleed formation is undesirable because it may require further treatment if it does not become reabsorbed by the ash matrix.

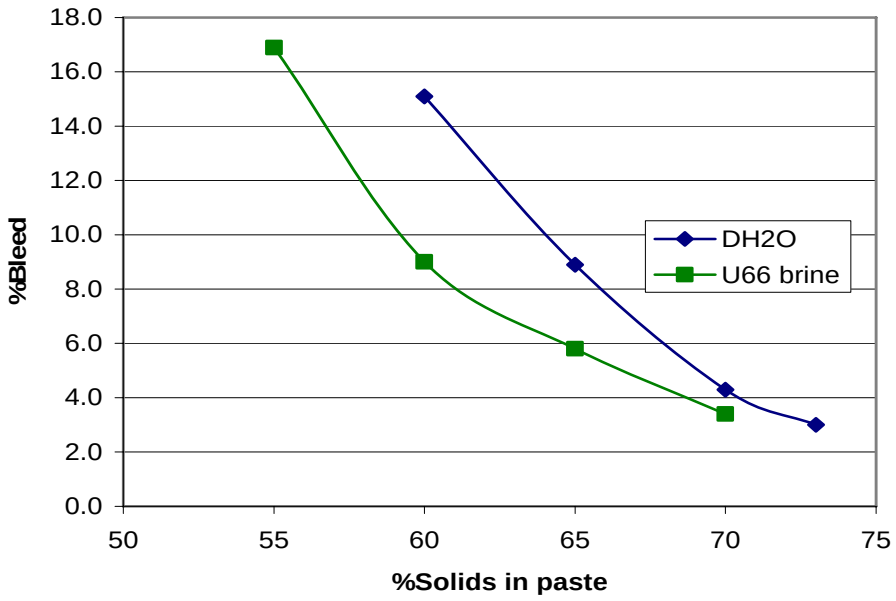

Fig. 5.1 Effect of salinity in bleed formation

Further details on the bleed behaviour (from both U66 brine and DH_2O pastes) as a function of time are illustrated in **Figures A2.1** and **A2.2** on pages 119 and 120.

It was noted that the settling of solids took approx. two hours in the case of U66 brine while only 45 minutes was taken with DH_2O. The absorption rate of the bleed was relatively higher with DH_2O. The quick settling and high bleed absorption rates might cause paste stiffening inside the pipes (i.e. during transportation). This can result in problems such as pipe blockages before reaching the disposal sites. Below is a table

that shows the difference between the pastes prepared from U66 brine and DH2O with the equivalent solids concentrations.

Table 5.1 Effect of salinity on paste behaviour

Paste with U66 brine	**Paste with potable water**
70% FA	70% FA
Slump = 0.39	Slump = 0.67
Settling rate = 2 hours	Settling rate = 45 minutes
Bleed absorption = 4 days	Bleed absorption = 1.2 days

Furthermore paste samples that were prepared with U66 brine showed better capability to withstand deviations in S:L ratios. A percent deviation from either side of the limit (suggested solids) with DH_2O produces a material that cannot be defined as a paste. However, the paste prepared using U66 brine provides a wider range. This makes the technology more robust and easy to operate once implemented. It has therefore been proven that brine composition plays a major role in paste behaviour implying that no standard recipe (i.e. S:L) can be given beforehand.

5.2 SLUMPING BEHAVIOUR

5.2.1 Evaluation of a Mini-Slump Test

A good correlation ($R^2 = 0.97$) was found between the standard cone and mini-slump tests, as illustrated in **Fig. 5.2**. The success of this evaluation implied that all slump tests could be conducted using only mini-slump test. The sample preparation would become a lot easier with smaller sample sizes. This directly relates to the challenges of sampling enough volumes of materials especially ash (as discussed in chapter 3). This was a value-adding discovery because it enabled the author to save up to six times on raw materials.

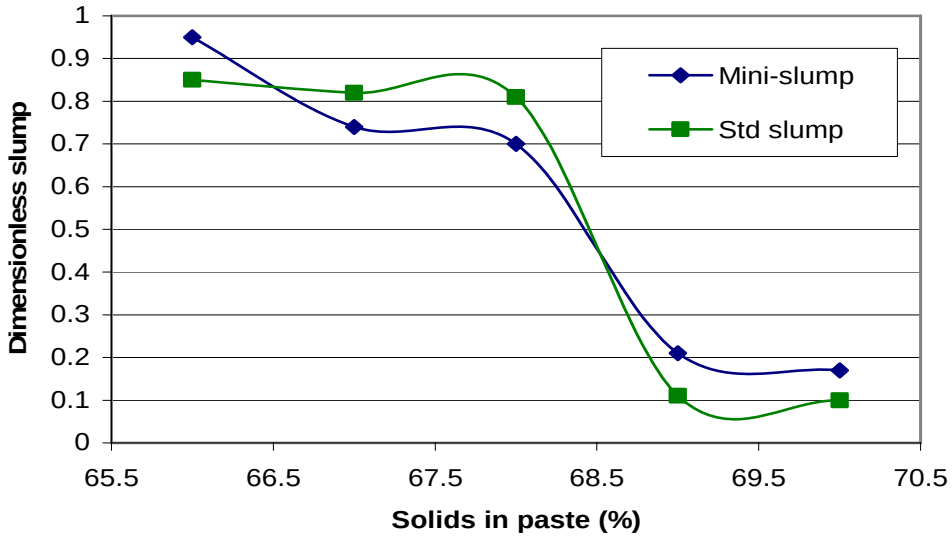

Fig. 5.2 The correlation between standard cone and mini slump tests

The paste with 68% solids seems to be a critical point separating the two sets of data. Below 68% the mini-slump test seems to underestimate the slumping while overestimation is observed beyond 68% solids. The results are also clearly illustrated using statistical methods as shown in **Fig. A3.1**on page 121. The observed difference might require further investigation; however, it was beyond the scope of this work.

5.2.2 Effect of Physical Ash Properties on Slumping

5.2.2.1 LOI content

It was found that the LOI values of a given sample were the same regardless of the temperature used. This made it possible to conclude that the LOI in the SASOL FA originates from unburned carbon since no proof of carbonate conversion was found (Heiri *et al.*, 2000). It was also discovered that the darker samples of FA had a higher LOI content which relates to unburned carbon (Bin-Shafique *et al.*, 2002). The fly ashes that are lighter in colour usually have a higher content of lime (Bin-Shafique *et al.*, 2002) prone to self-cementing.

The values of LOI are well within the international standards. The implications are that the combustion efficiency is good

considering the fact that low-grade coal is utilised (van Dyk *et al.*, 2006).

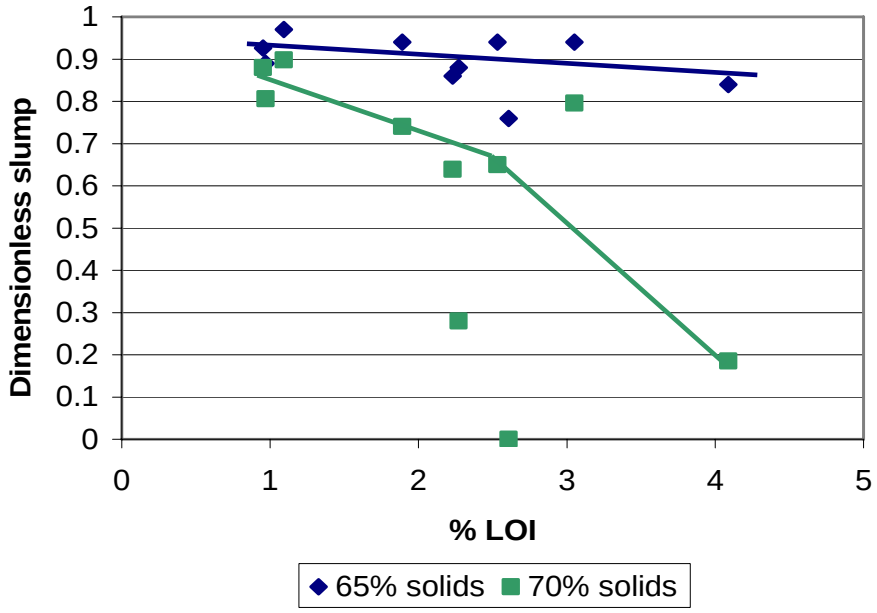

Fig. 5.3 Relationship between mini-slump and LOI

The increasing LOI values of fly ash reduced the slumping behaviour of pastes. This implies that more energy will be required during transportation, which is an additional cost. The effect of LOI was predominant in pastes containing higher solid concentrations (e.g. 70%). However, the effect of LOI in slumping behaviour was almost negligible in pastes with lower solids concentrations such as 65%. This is shown in **Fig. A3.2** on page 122. This independently suggests that the paste with relatively higher solids concentrations will be sensitive to the

changes in the ash properties such as LOI. This may therefore pose operational problems.

5.2.2.2 Fineness

The slumping behaviour was affected by fineness as illustrated in **Fig. 5.4** below.

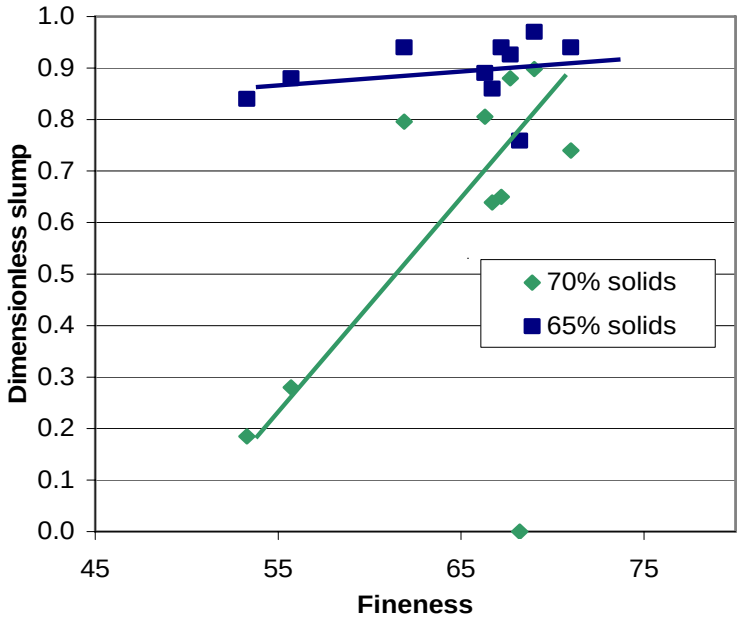

Fig. 5.4 Relationship between increase in fineness and slumping

The fly ash samples with higher degrees of fineness exhibited better slumping behaviours in pastes. This observation is important for the possible minimisation of transportation costs, and can be attributed to the lubrication effect resulting from the spherical particles (Ferraris *et al.*, 2001; Chindaprasirt *et*

al., 2005; Stropnik and Južnič, 1988). The effect of fineness was predominant in pastes with higher solids concentrations e.g. 70%. The effect in slumping was little in pastes containing lower solids concentrations e.g. 65%. The paste containing higher solids is largely affected by the lubrication caused by fineness.

5.2.2.3 Time dependence

No change in the revolutions per minute of the mixer was observed over time. This could be due to either a high torque of the mixer or small paste volumes that were used.

The generated data from the three different paste samples are shown in **Fig. 5.5**. The effect of the salinity of the liquid medium on the stiffening process was demonstrated. The paste prepared from fly ash and DH_2O showed a faster rate of stiffening than that from fly ash and U66 brine. A dimensionless slump of 0.15 was obtained after approximately 94 hours with U66 brine while it took 48 hours to reach the same consistency with DH_2O. These observations have important practical implications. Firstly, it appears that the chemical composition of the brine affects the hydration process of the paste by

delaying the reactions responsible for stiffening. Secondly, it implies that pipeline blockages due to in situ stiffening of the paste will be less of a problem for fly ash pastes when liquid media such as U66 brine are used for paste preparation.

The reactions responsible for the observed behaviours are postulated to be similar or even identical to those found in the hydration of cement (Backe *et al.*, 1999; Pagé and Spiratos, 2000). They may include phenomena such as wetting of fly ash particles and surface hydration which are exothermic (Pagé and Spiratos, 2000). The presence of certain ions in the U66 brine could have the same effect as plasticizers which retard the hydrations reactions (Pagé and Spiratos, 2000; Asavapisit and Cosanavit, 2004; Tommaseo and Kersten, 2002).

The use of sieved weathered ash instead of fly ash produced totally different result with U66 brine. The paste was segregating although S:L ratio was optimised. A gradual decrease in slump was observed that could be attributed to uncontrollable evaporation. The fact that the rapid decrease in slump observed with fly ash was not observed with weathered ash supports the notion that hydration reactions are responsible for the time dependence of the slumping behaviour in paste.

This could be explained by the fact that weathered ash had already reacted and hydration reactions had possibly reached equilibrium (Pretorius and Nieuwenhuis, 2002). The use of weathered ash has a potential to prolong the transportation period of paste. However, careful consideration of other factors may be required e.g. compressive strength and permeability of the resultant pastes.

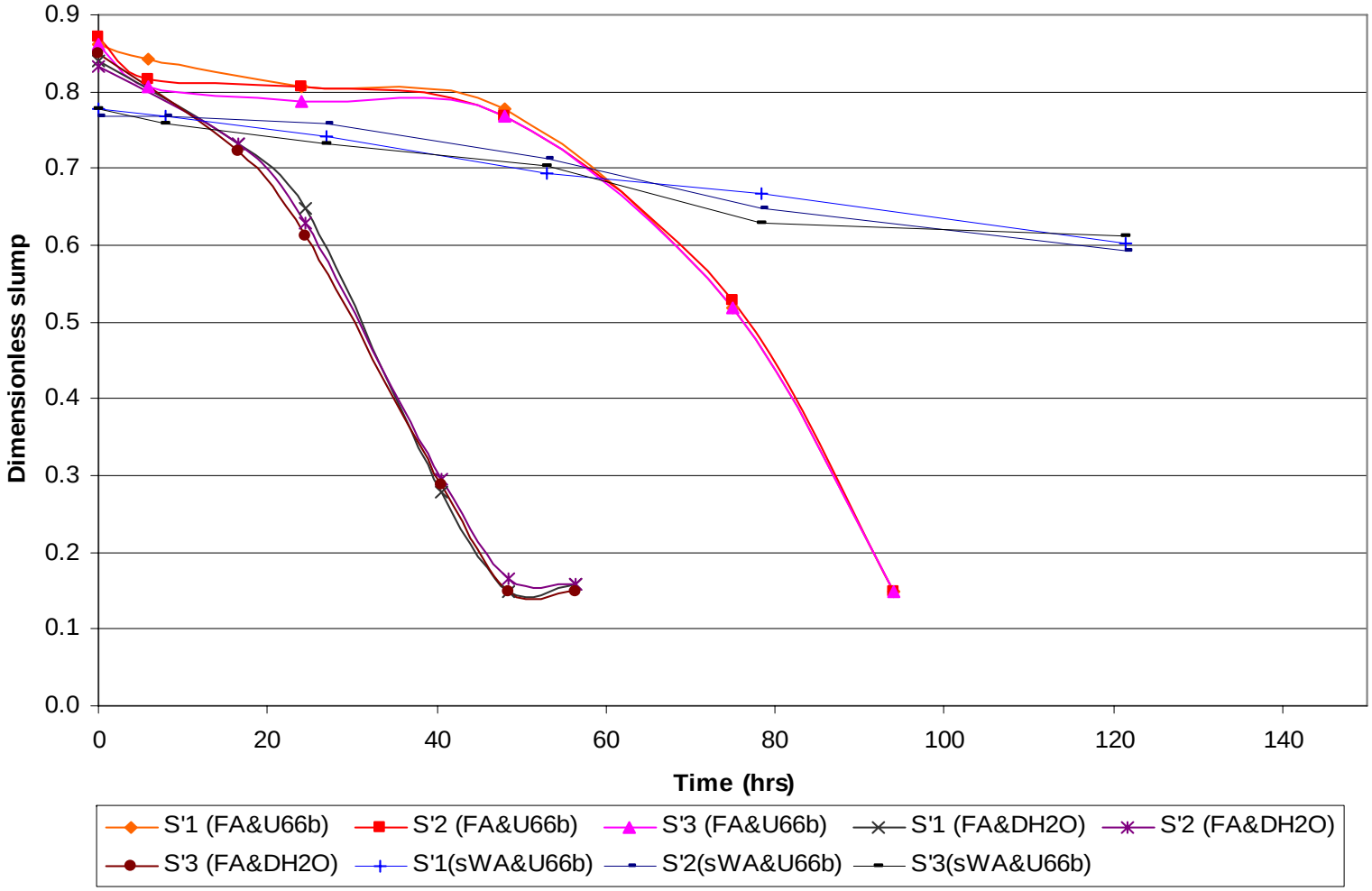

Fig. 5.5 Time dependence of slump per set of materials

The observations clearly demonstrated that the liquid medium used during paste preparation plays a major role in the transportability of paste. The paste prepared using fly ash and U66 brine can easily be pumped within 50 hours of preparation for 3-4 km (Newman *et al.*, 2001). The use of distilled water reduces the pumping allowance by almost 80%, meaning transportation must occur within 10 hours of paste preparation.

5.3 EFFECT OF DIFFERENT BRINES ON PASTE

5.3.1 Salts Retention and Slumping Behaviour

A workable paste was found between 60% and 70% solids concentration for various brines. However, the optimum S:L ratios were similar but not close enough to make a generalisation. The implications are that optimisation is essential for each brine type and FA. The optimum ratios were determined for each set of materials and the data illustrated are summarised in **Table 5.2**. The optimum point was based on the consistency and slumping of paste.

Table 5.2 Data on pastes from various brines

Brine	Initial TDS (g/l)	Final TDS (g/l)	% retained	% S: L	Slump
FAM	6.3	1.3	78	68	0.82
TRO (U69)	8.4	0.6	93	68	0.88
EDR	12.0	0.9	92	68	N/A
U66	60.8	5	95	68	0.82
SD3	115.0	10	91	65	0.86
SLF	274.0	30	89	64	0.84
BEN	444.0	40	91	64	0.81

It was furthermore discovered that the salt load (i.e. TDS concentration) of brine does not govern salt retention. For instance, FAM and TRO brines have the closest initial salt loads but retentions were extremely different (i.e. 78% versus 93% respectively). Conversely BEN and SLF had the highest initial salt loads but didn't exhibit the best salt retention. This implied that there could be a limit in the amount of salts that can be retained in paste. The overall deduction from **Table 5.2** and **Fig. 5.6** is that the more salts are added during paste preparation the more will leach out.

There is therefore a potential to make blends of brines to give both a favourable chemical composition and salt load. The understanding of ions that positively affect paste technology can be conducted as a study on its own.

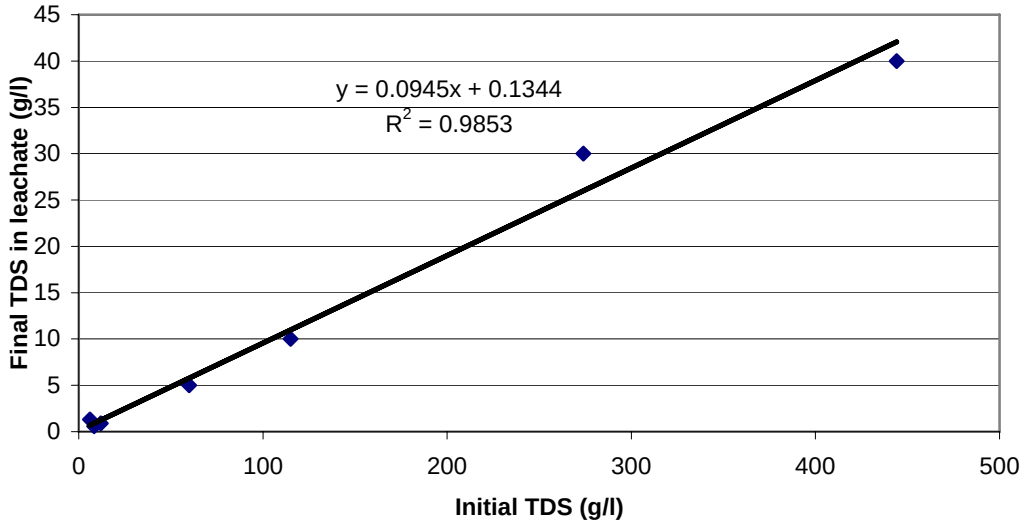

Fig. 5.6 Relationship between initial and final TDS

5.3.2 The Kinetics of Leaching and Role of Eluant

The readings of both pH and conductivity (EC) were regularly taken until equilibrium was established. The term equilibrium refers to a state where there were no further detectable changes in the values of pH and EC. The results in **Fig. 5.7** indicate that salt remobilisation occurs within the first 6 days when paste interacts with water. No evidence of further leaching was obtained by leaving the experiment for a total of 14 days.

This is, however, not the case if an eluant is replaced with a fresh one after reaching equilibrium. Previous work showed that equilibrium can be reached more than one if an eluant is replaced. (Details of this work are not discussed in this dissertation). Of particular interest, was the fact that TDS and EC decreased after each equilibrium, as illustrated in **Fig. 5.8**. It can be concluded that the release of salts is infinite if leaching media are replaced with less saline ones. Furthermore a steep increase in EC was observed with a peak after approx. 18 hours of leaching, which was followed by a decrease in EC before equilibrium. The trend was repetitive in the three cases as shown in **Fig. 5.8**. The reason behind this trend was not

investigated but further research on this issue could lead to a minimisation of the leachability of paste.

Results in **Fig. 5.7** also show that brine chemistry does not affect reaction kinetics of remobilisation because it took about 120 hours to reach equilibrium regardless of the brine used. This may, however, change in very old paste samples (e.g. 6 months old) due to different secondary phases (Chen *et al.*, 2004).

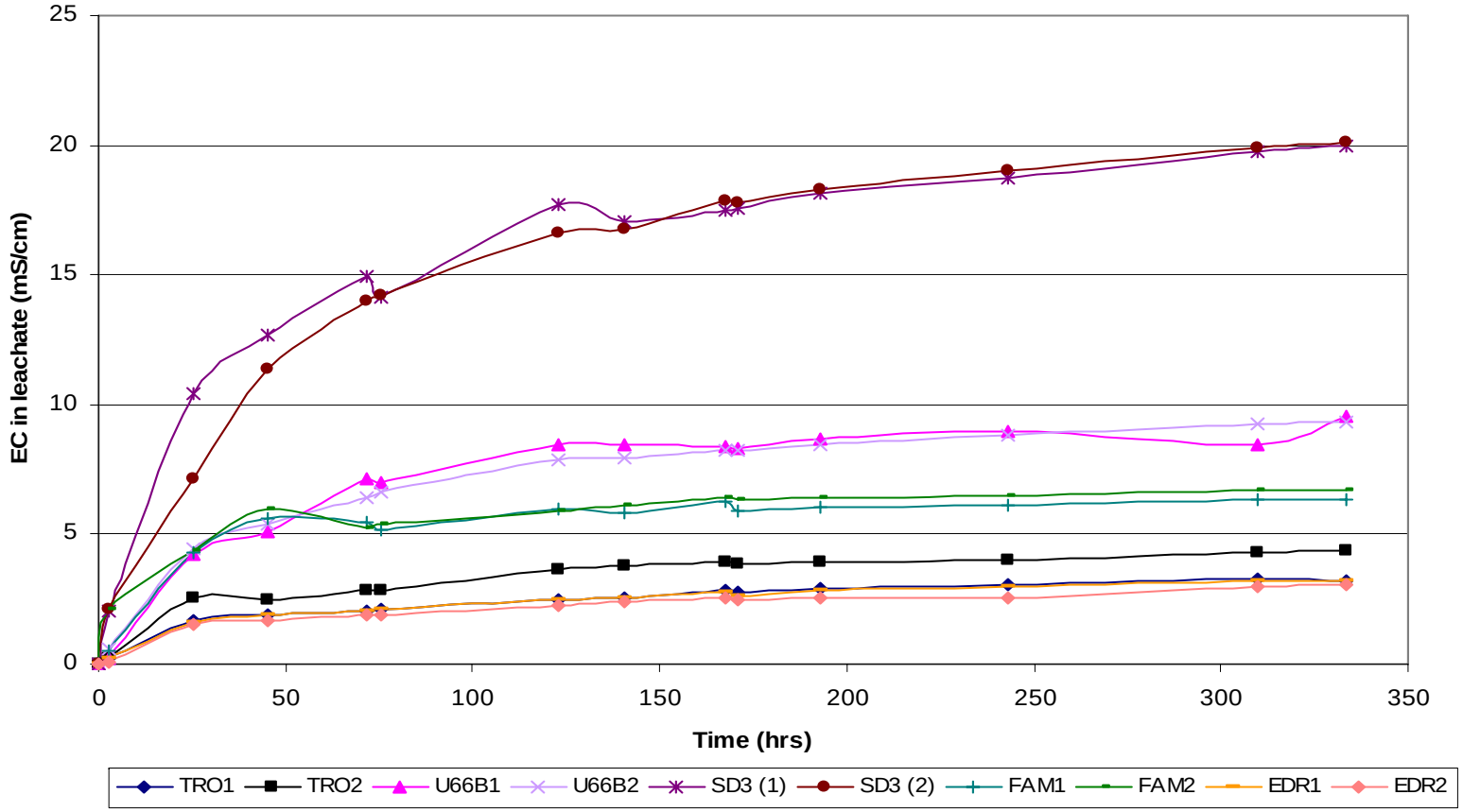

Fig. 5.7 Conductivity plot against time of leaching for paste from various brines

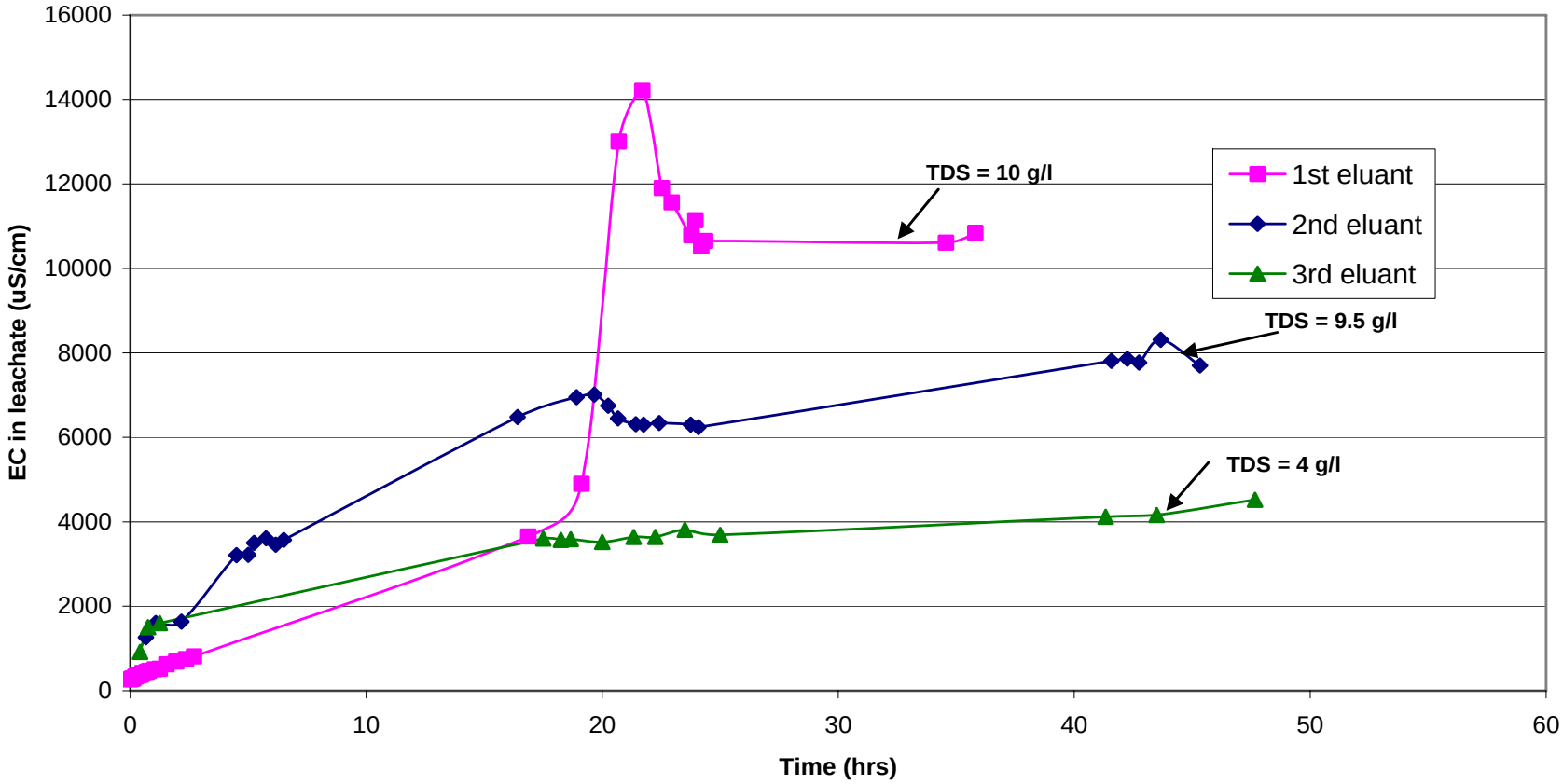

Fig. 5.8 Effect of replacing eluant on remobilisation

5.4 EFFECT OF ADDITIVES

5.4.1 Sieved Gasification Ash

The addition of SGA proved to remedy the cracking of paste prepared from FAM at as low as 17% and 25% additions. **Plate 5.1** below shows how cementation improved with SGA additions.

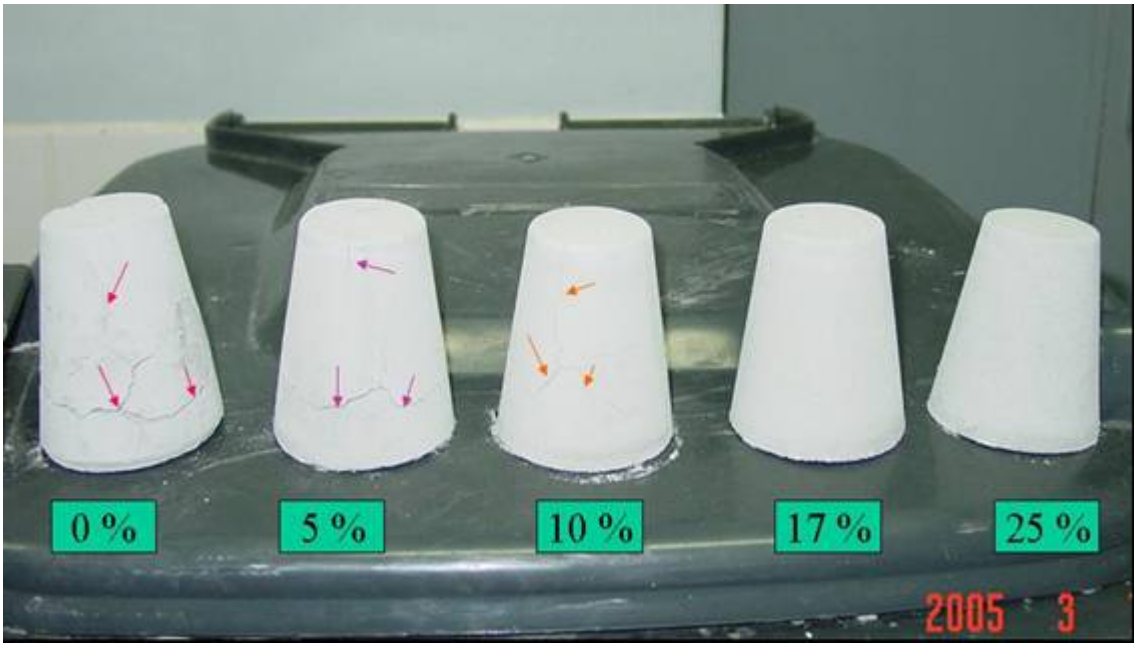

Plate 5.1 Diminishing cracks per increased SGA addition

The samples with 0% and 5% SGA collapsed immediately when placed in 1.3 of DH_2O. The samples with 10% SGA were slightly cracked but they did not collapse in water while those containing 17% and 25% SGA neither cracked nor collapsed.

This observation can be attributed to cementatious binding (Wilk, 1999). Furthermore the increase in SGA additions was directly proportional to the increase in salt retention. This

conclusion was based on EC and TDS trends. The use of SGA in paste will potentially improve the cementatious properties of paste and minimise the environmental impact. The abovementioned findings are summarised in **Fig. 5.9**, with TDS values written on the graph.

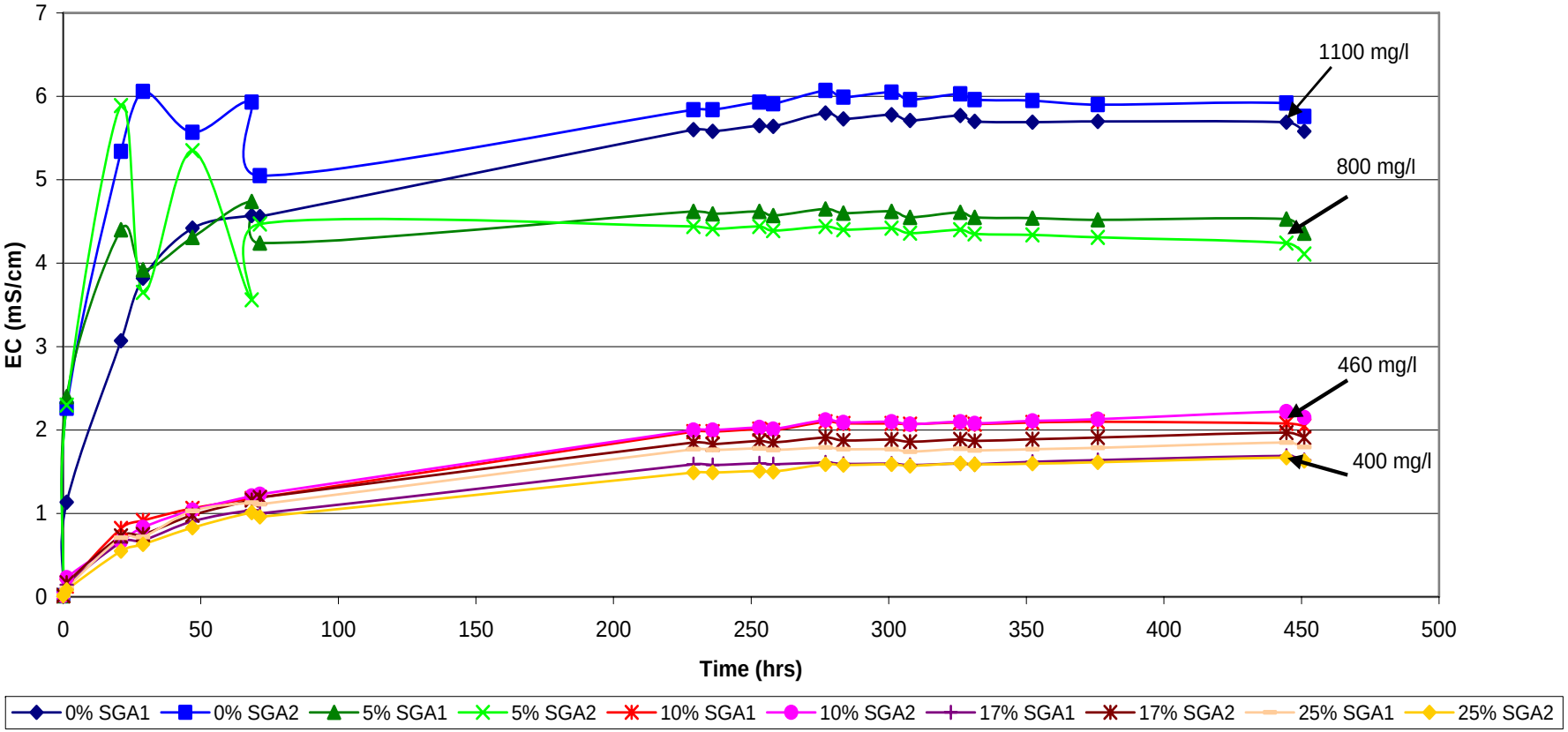

Fig. 5.9 Conductivity plot against time under various GA additions

5.4.2 Incineration Ash (IA)

The samples were brittle during remobilisation with an exception of the one containing 15% IA. This gave an indication that incineration ash has a potential to enhance binding of wastes in paste and improve its strength.

The equilibrium was established after approx. 550 hours of leaching based on EC trend illustrated in **Fig. B1.1** on page 123. The leachate samples with IA additions were approx. 5 times lower in TDS than the control, see **Fig. 5.10** below.

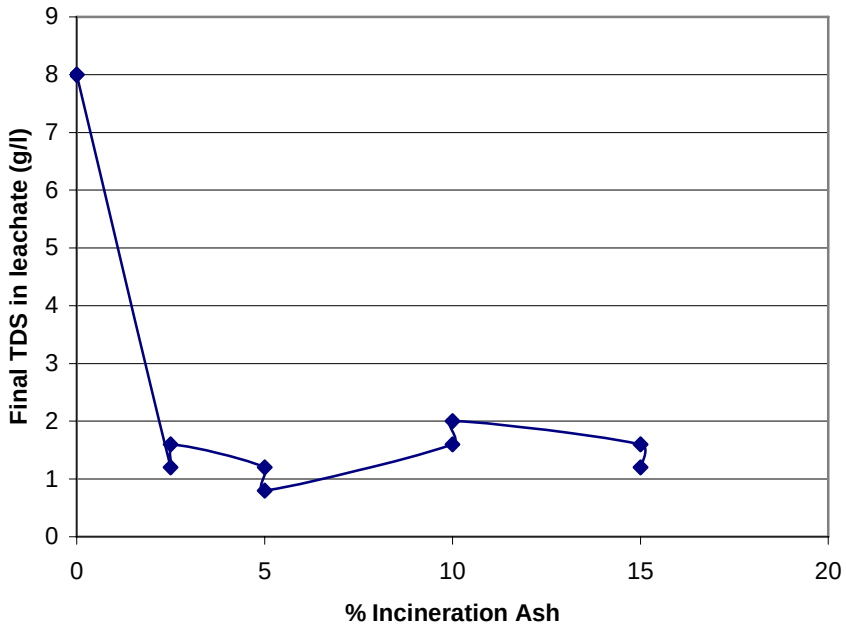

Fig. 5.10 Effect of incineration ash on salt retention

Low TDS values imply reduction in leachability and high salt retention. It can therefore be concluded that IA has a potential to improve salt retention based on these results.

5.4.3 Lime (CaO) as an Additive

The paste samples with lime additions were cracked but didn't collapse when immersed in DH_2O. This observation suggests that lime addition could play a role in binding and strength development (Bin-shafique *et al.*, 2002; Joshi *et al.*, 1993). These materials felt stronger than the rest of the samples although no scientific method was applied. It took approx. 550 hours to reach equilibrium in terms of EC graph, see **Fig. B1.2** on page 124. There was approx. eight times improvement in the leachate quality based on TDS results (see **Fig. 5.11** below).

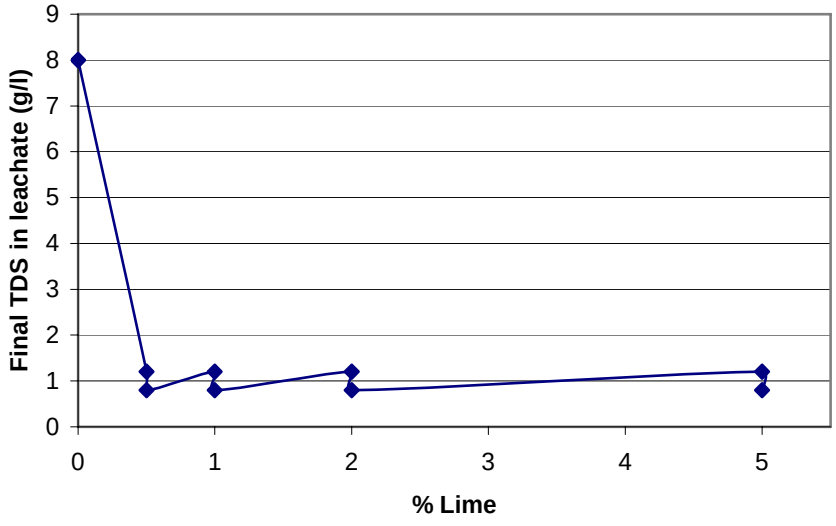

Fig. 5.11 Effect of lime on salt retention

Previous experiments (not described in this dissertation) where 5% and 10% lime were added during paste preparation (68% solids and U66 brine), showed enormous reduction in permeability (see **Table 5.3**).

Table 5.3 Effect of lime in permeability

% CaO added to FA	Curing time (days)	Permeability (cm/s)
0	5	2.0E-04
0	9	4.0E-05
0	27	6.0E-06
5	13	6.0E-06
10	13	7.0E-08

The permeability coefficient of 6.0E-06 cm/s was obtained after approx. four weeks in a control while it only took two weeks with 5% lime addition. The addition of 10% lime reduced the permeability by 100 times in two weeks time. This was in support of the work reported in literature (Joshi *et al.*, 1993).

5.4.4 Portland cement (OPC) as an Additive

The results are similar to those obtained with lime. Data are shown in **Fig. 5.12** below and **Fig. B1.3** on page 125.

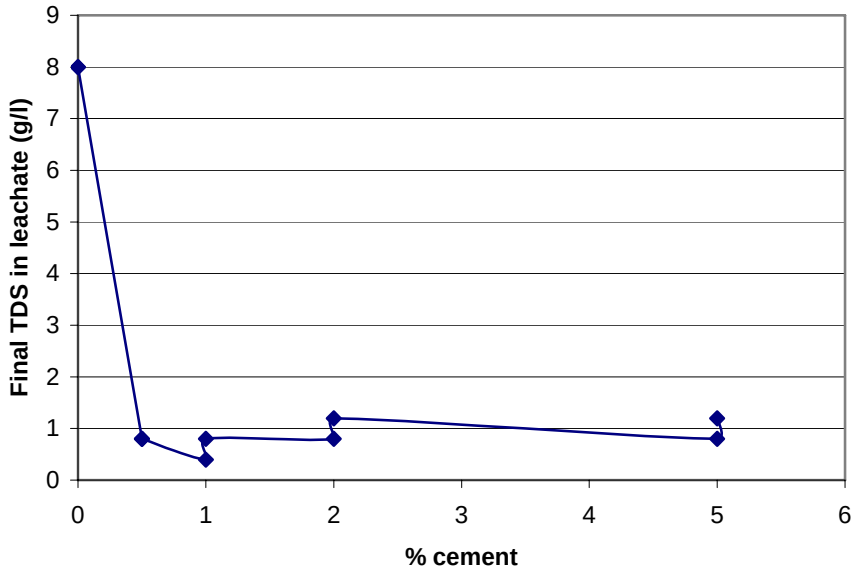

Fig. 5.12 Effect of cement on salt retention

5.4.5 Silica Fume (SF)

The use of SF led to an increase in water demand which was proportional to the amounts of SF added to FA (Pagé and Spiratos, 2000). SF is a very fine material and its addition could result in an increase in the total surface area of FA and hence elevate the water demand (Ferarris *et al.*, 2001; Pagé and Spiratos, 2000).

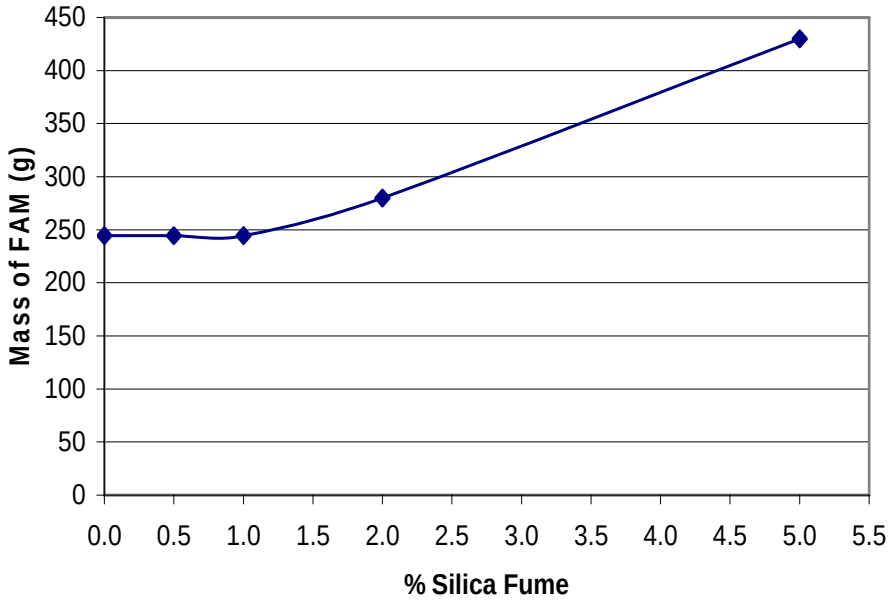

Fig. 5.13 The increase in liquid mass against SF additions

The increase in water demand can individually be perceived as a possible solution to bleed handling. This can be advantageous in cases where there is little ash available to handle large volumes of brine.

It was, however, observed that the texture of paste changed to a sticky material like clay with relatively higher SF additions ($\geq$ 2.5%). This could introduce blockage problems during paste transportation. The optimum salt retention was found between 0.5% and 1% SF additions, which was approximately eight times better than the control (see **Fig. 5.14)**.

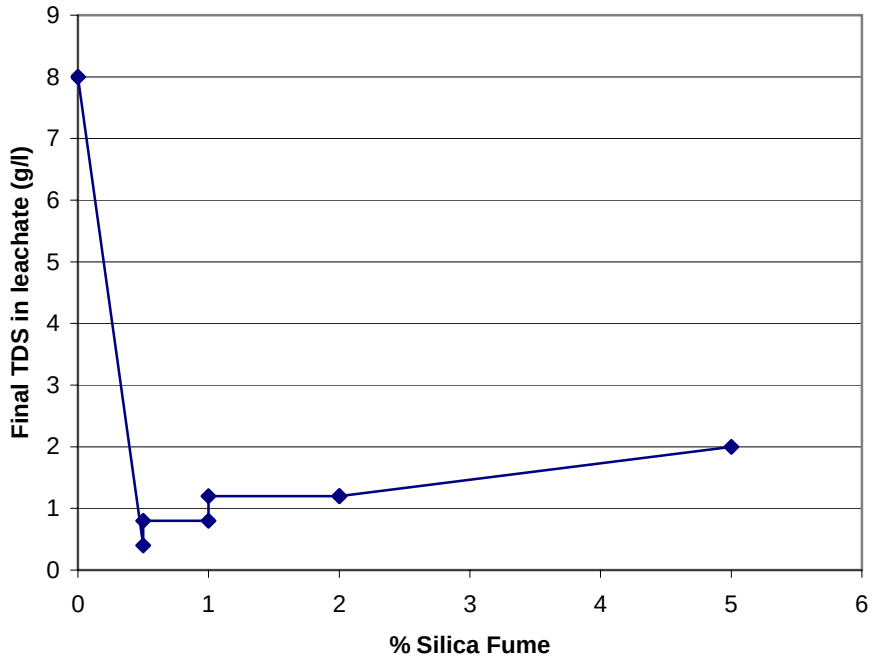

Fig. 5.14 Effect of silica fume on salt retention

The increase in TDS observed at 5% SF was also augmented by the EC graph shown in **Fig. B1.4** on page 126. It was observed that SF additions have a tendency to increase the permeability (see **Table B1** on page 126). These observations are in accordance with those made by Ferraris *et al.*, 2001. The increase in permeability is often undesirable because water gets access to the ash matrix and chances of salt remobilisation become higher.

5.4.6 A Comparison of Different Additives

There is a huge potential to utilise some of the SASOL wastes (namely incineration ash and gasification ash) as additives during paste preparation. An improvement of approximately 80% in salt retention was observed with 5 – 10% additions of IA. Conversely the addition of finer gasification ash also increased salt retention by approximately 65% at a dosage of 25%. The improvement in salt retention using SASOL solid wastes was in the same degree as that observed when commercial additives (such as lime and cement) were tested in the range of 0.5 – 1% additions. The addition of silica fume cannot be encouraged within current information.

5.5 EFFECT OF SURFACE AREA ON REMOBILISATION

5.5.1 Does Curing Time Affect the Dependence on Surface Area?

Diff represents the results obtained from intact pastes -while **Diss** refers to those that were pulverised before interaction with water. The data illustrated in **Fig. 5.15** shows a good correlation of TDS determined from the leachate samples representing the two scenarios.

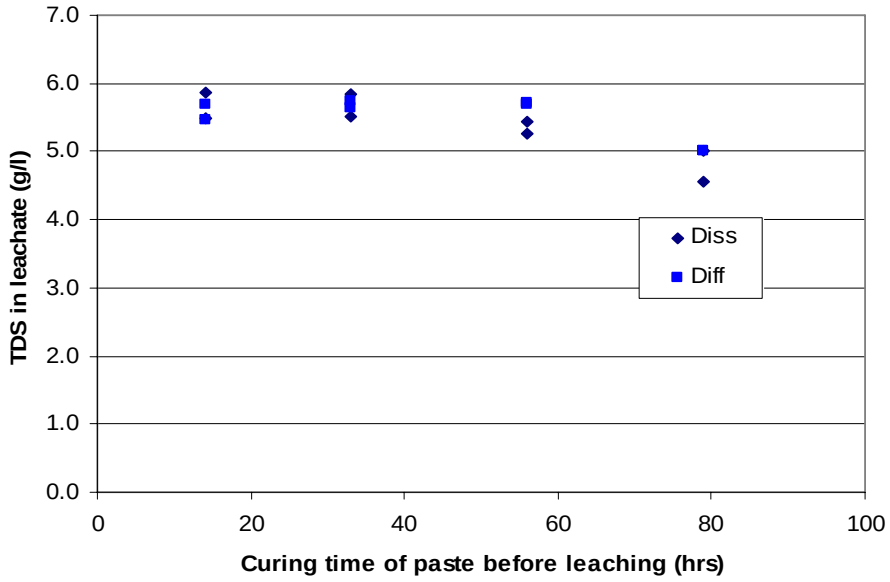

Fig. 5.15 Testing surface area against curing time

The statistics showed that there was no significant difference in TDS from the two scenarios over time (see **Fig. B2.1** on page 127). It was expected that no pozzolanic reactions would have occurred in the early stages of curing hence most salts could be physically trapped. However with increased curing times chemical retention would also be present. Furthermore monovalent cations may behave differently depending on surface exposure since they are water-soluble. The monovalent species were expected to be remobilised in dissolution experiments because the ash matrix was destroyed and limited physical encapsulation would remain. The shorter curing times such as two weeks and below were expected to give similar

leachability. The lack of a difference between leaching a sample with a large or a small surface area over time implies that the retention is mainly chemical bonding. It is therefore postulated that the reaction kinetics of hydration are faster i.e. may occur in a matter of weeks. This is only based on the observed trend and requires further investigation.

5.5.2 Triplets of 6.5 months old paste (U66 brine)

The data of EC, and TDS were plotted after equilibria were established. The triplicates of dissolution and diffusion are represented by Diss1 to Diss3 and Diff1 to Diff3 in **Figures 5.16 & 5.17**. The results showed that surface area of paste exposed to water does not affect the reaction kinetics of salt remobilisation because equilibrium was established at the same time. It was also deduced that the extent of salt remobilisation is independent of surface area since final TDS was equivalent in both scenarios. The findings are illustrated in **Figures 5.16 & 5.17**, which are in accordance with statistical results shown in **Fig. B2.2** on page 128. It took approx. 10 days for equilibrium to be reached.

An initial release of salts is rather fast and reaches a peak after 100 hours of leaching. This was followed by a small reduction in TDS and EC before equilibrium was reached. It took approx. 200 hours to reach equilibrium (see **Figures 5.16 & 5.17**). The mechanism by which salts are released is similar to that discussed in section 5.3. The pattern is the same as that shown in **Fig. 5.8**.

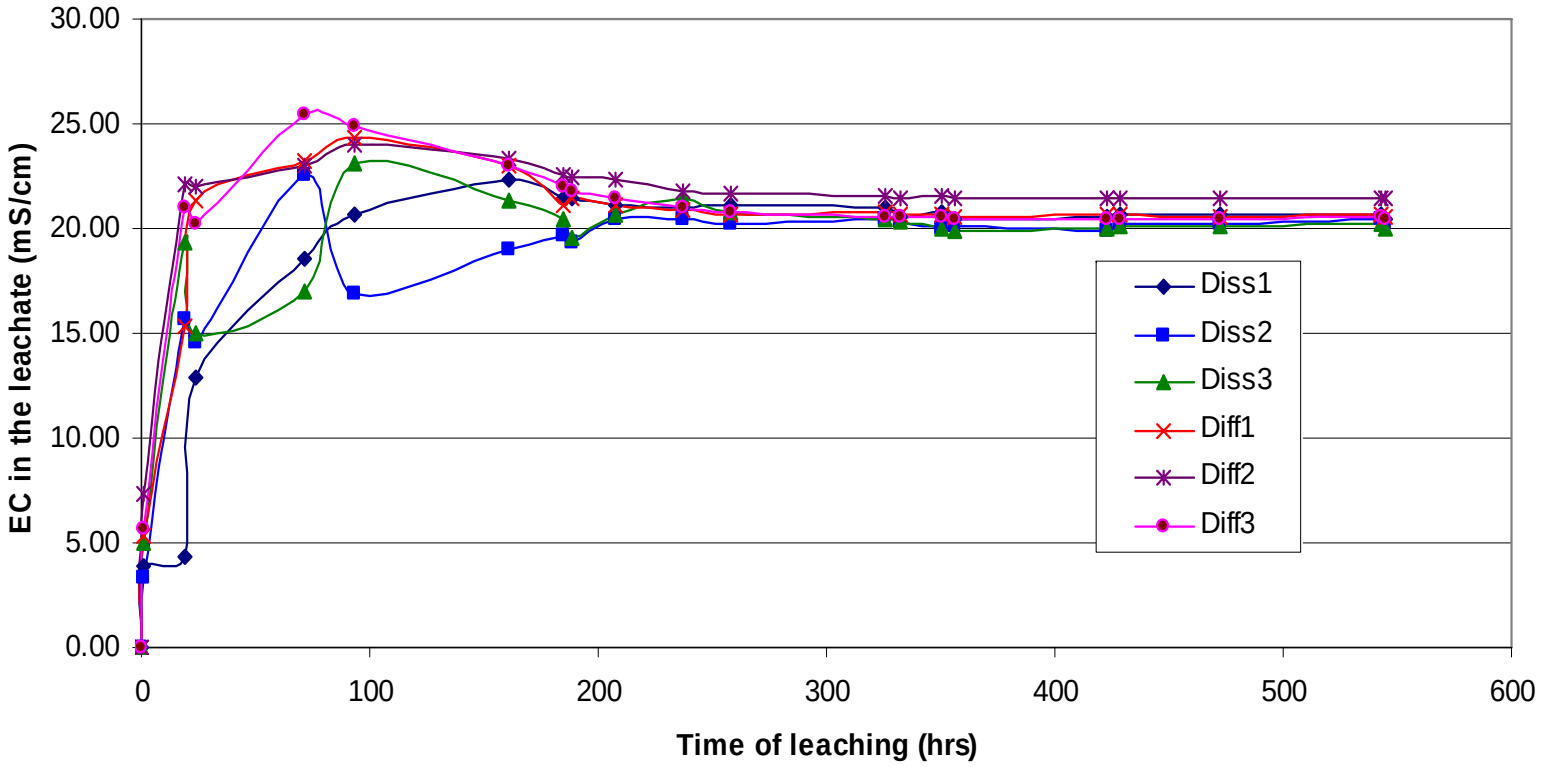

Fig. 5.16 Conductivity as a function of time

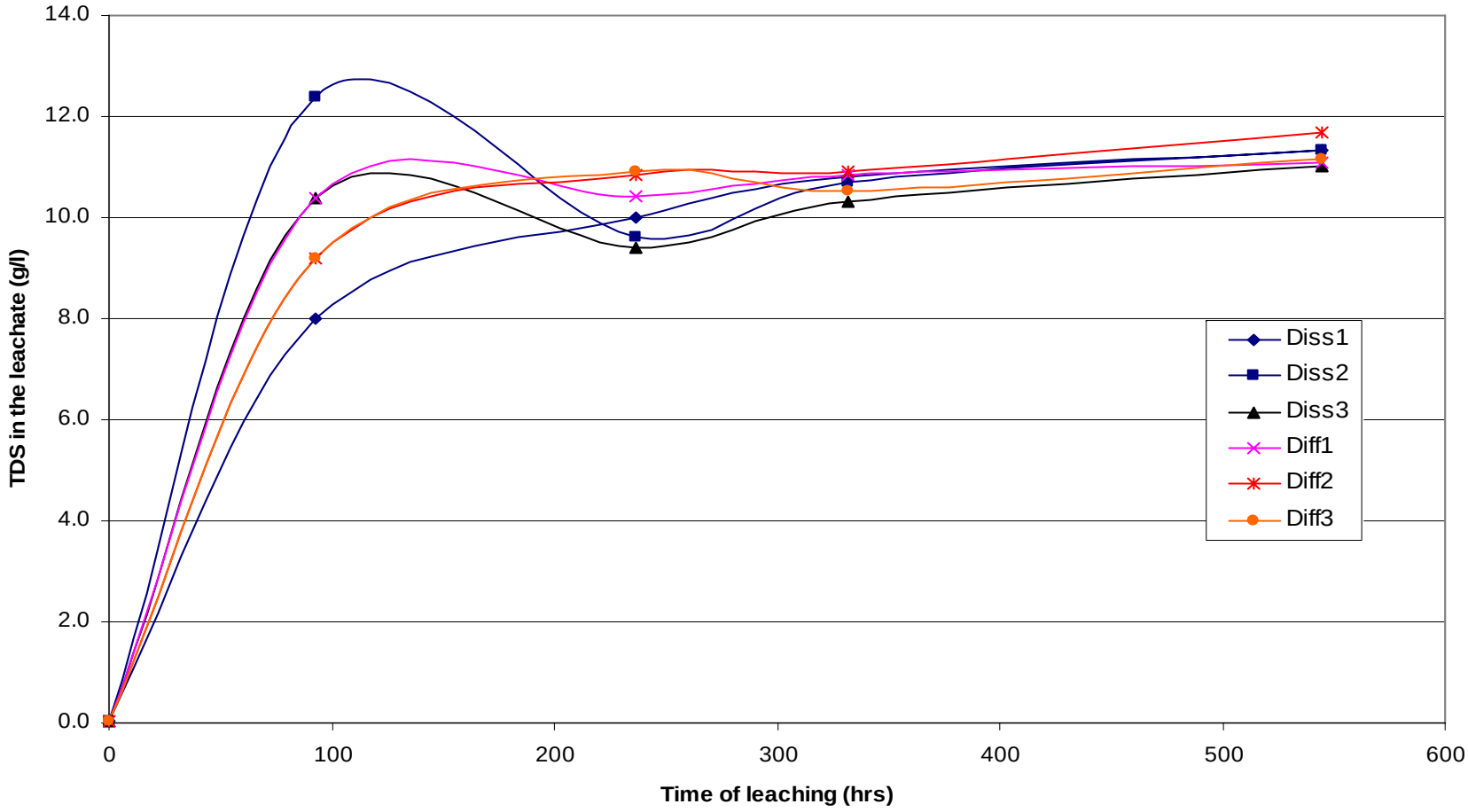

Fig. 5.17 Plot of TDS as a function of time

The analysis of leachates showed similar results for dissolution and diffusion as illustrated in **Table 5.4**.

Table 5.4 A summary of leachate analysis

sample	TDS (g/l)	EC (mS/cm)	Ca (mg/l)	Na (mg/l)	K (mg/l)	Cl (mg/l)	SO42- (mg/l)
Diss1	10.49	15.15	151	1900	380	1767	4200
Diss2	10.76	14.81	163	1900	360	1866	4200
Diss3	10.53	14.64	145	1850	340	1826	4200
Diff1	10.43	15.08	110	1900	410	1945	4100
Diff2	10.78	15.59	149	1950	420	2223	4700
Diff3	10.11	14.99	149	1900	390	2144	3900

The diffusion test has a small surface area of paste exposed in water hence stands a better chance to retain the salts that are physically trapped in the paste matrix (Klem and Bhatty, 2002; Wilk, 1999). The difference was expected in samples with longer curing times when pozzolanic reactions are taken into account. The lack of such a difference over time led to an indication of how the salts are retained in paste. It was therefore postulated that chemical bonding is a major mechanism by which salts are retained in ash pastes rather than physical encapsulation.

5.6 EFFECT OF CURING ON PERMEABILITY OF PASTE

The permeability results of pastes between 5 and 27 days of curing are illustrated in **Fig. 5.18**. It was discovered that longer curing times lead to a less permeable paste, which is a desired property. There was a quick reduction in permeability between 5 and 10 days of curing, which was followed by a slow decrease up to 27 days.

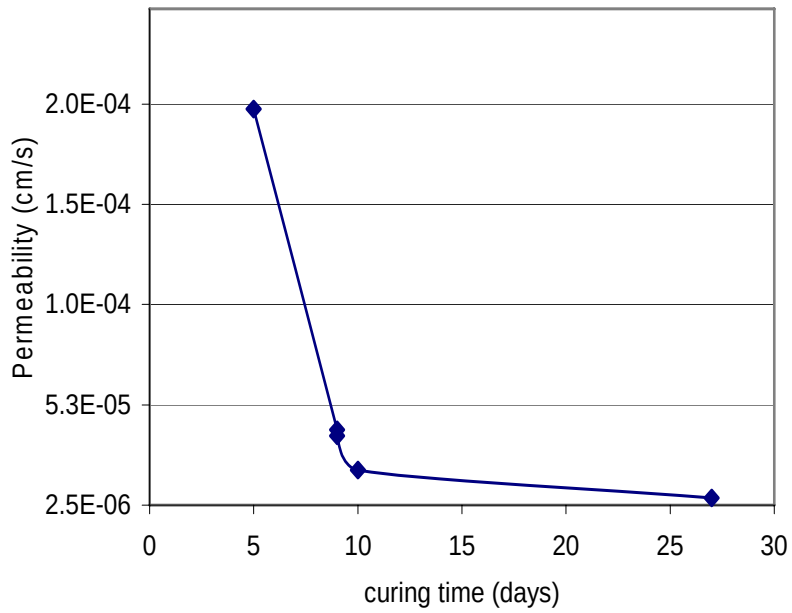

Fig. 5.18 Permeability as a function of curing time

A curing time obtained after 27 days was almost 10 times lower than that obtained after five days. The permeability values ranged from 2 x 10^{-4} to 6 x 10^{-6} cm/s. The effect of curing was

considerable and the permeability values were similar to those of a silt or a silty clay soil (Josh *et al.*, 1994; Benzaazoua *et al.*, 2004a).

The study has given some insight and deeper understanding of the paste technology. The points discussed in this chapter have led to conclusions and recommendations for further research which are discussed in the next chapter.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary of the Findings

- The results have shown that the transportability of paste is affected by physical properties of fly ash such as LOI and fineness. In addition, pastes with higher solids concentrations were more susceptible to the deviations in the physical properties of fly ash. This sensitivity requires close monitoring of the process which implies additional man-power and an increase in running cost thereof. The pumpability of paste with relatively higher solids concentrations (e.g. 70%) will also require more energy which is another cost implication. Conversely the paste containing less solids concentration such as 65% will be less sensitive to the changes in physical properties of fly ash and pumpability will require less energy. Hence it will be better to operate at lower S:L ratios.

- The liquid medium used during paste preparation plays a major role in the settling and slumping of paste. It was observed that salinity is one of the factors that affect the settling rate. The availability of various brines within Synfuels provides an opportunity to prepare blends that will provide suitable settling of paste. Furthermore it was observed that the salinity affects the transportability of paste. The use of a suitable liquid medium could prolong the transportability of a paste to a disposal site, without any addition of plasticizers. In addition blockages in pipes can be controlled by influencing the settling rate. These factors could have economic benefits. The findings also showed that salt retention was dependent on the chemical composition of the brine rather than the salt load (i.e. TDS). However there seems to be a limit in the amount of salts that can be retained in paste. This makes it possible to blend streams with an intention of achieving a suitable chemical composition and salt load. The understanding of the role that various ions play during the paste formation will require further research. The results

from that study are likely to broaden the applications of paste technology.

- There is a huge potential to utilise some of the SASOL wastes like incineration ash (IA) and gasification ash, as additives during paste preparation. An improvement of approximately 80% in salt retention was observed with 5 – 10% additions of IA. In addition finer gasification ash also increased salt retention by approximately 65% at a dosage of 25%. The improvement in salt retention using SASOL wastes was comparable to commercial additives such as lime and cement. These were tested in the range of 0.5 to 1% additions. The addition of silica fume cannot be encouraged with the current information. The potential use of SASOL solid wastes will address the salt problem and provide cost benefits in terms of commercial additives that could be required.

- The studies showed that there was no measurable difference between diffusion and dissolution in terms of leachate quality and kinetics of salt release. It was postulated that the mode of retention is due to

chemical bonding rather than physical encapsulation. The verification of this postulate needs further research. The understanding of the retention mechanism of salts in paste is critical to determine its sustainability.

6.2 Recommendations

The intention of this investigation was to assess the technical feasibility of paste technology. The results obtained during the study have enabled the author to recommend positive or favourable conditions for a paste technology. However, there is a need to continue with the research since insufficient data is available for full-scale implementation.

Suggestions for future work in this project include;

- Undertaking a study to determine the hydration reactions and kinetics thereof. This could lead to an understanding of ways to accelerate the hydration reactions e.g. by use of additives or control of temperature.

- Pursue solid phase analyses on pastes using CCSEM. Successful identification of the secondary minerals such as ettringite and Friedel's salt could improve the confidence to implement this technology and environmental impacts can be predicted.

- Strength determination, which uses less pressure than in concrete testing, should be used.

- Construction of a pilot plant would improve data collection over a defined period of time. The laboratory study does not accurately simulate the field conditions.

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APPENDIX A

ADDITIONAL DATA AND RESULTS ON PUMPABILITY

A1: THE CHEMICAL COMPOSITION OF BRINES

A2: THE ROLE OF SALINITY IN BLEED BEHAVIOUR

A3: STATISTICS ON SLUMPING

A1: THE CHEMICAL COMPOSITION OF BRINES

TABLE A1: Typical composition of brines at SASOL Synfuels

Component	Units	U66	EDR	TRO	FAM	SD3	Sulfolin	Benfield
pH	--	5.5	7.4	6.5	12.1	8.8	8.2	10.9
P Alkalinity	mg/l as CaCO3	0.0	N/A	N/A	1271.0	367.0	N/A	880
M Alkalinity	mg/l as CaCO3	0.0	253.1	50.9	1381.5	916.0	27900	1090
Chloride	mg/l	32342		1216	929.0	34344.0	N/A	500
Fluoride	mg/l	6.9	2.6	12.7	26.6	39.2	100	10
Calcium	mg/l	850.0	430	396.6	437.5	2030.0	1500	20
Chromium	mg/l	N/A	< 0.1	N/A	<0.1	<0.1	N/A	N/A
Iron	mg/l	2.0	< 0.1	N/A	0.2	0.5	15	50
Potassium	mg/l	2160	17.2	94.8	131.9	415.0	250	126890
Magnesium	mg/l	50.0	300	190.3	3.2	1540.0	25	N/A
Manganese	mg/l	N/A	< 0.1	N/A	<0.1	5.0	N/A	N/A
Sodium	mg/l	42112	2425	1183.2	1153.3	12850.0	85400	1427
Strontium	mg/l	N/A	< 0.1	N/A	26.8	28.1	N/A	N/a
Ammonia	mg/l	N/A	N/A	N/A	2750.0	N/A	N/A	N/a
Vanadium	mg/l	58.2	< 0.1	N/A	<0.1	N/A	900	3641
Sulfate	mg/l	19800	7481	3760	2305.0	5250.0		0.00
TDS	mg/l	60800	11682	8400	6333	113958	274400	444000
Conductivity	mS/cm	81900	16.7	14.8	7.3	123500.0	200.0	244000

A2: THE ROLE OF SALINITY IN BLEED BEHAVIOUR

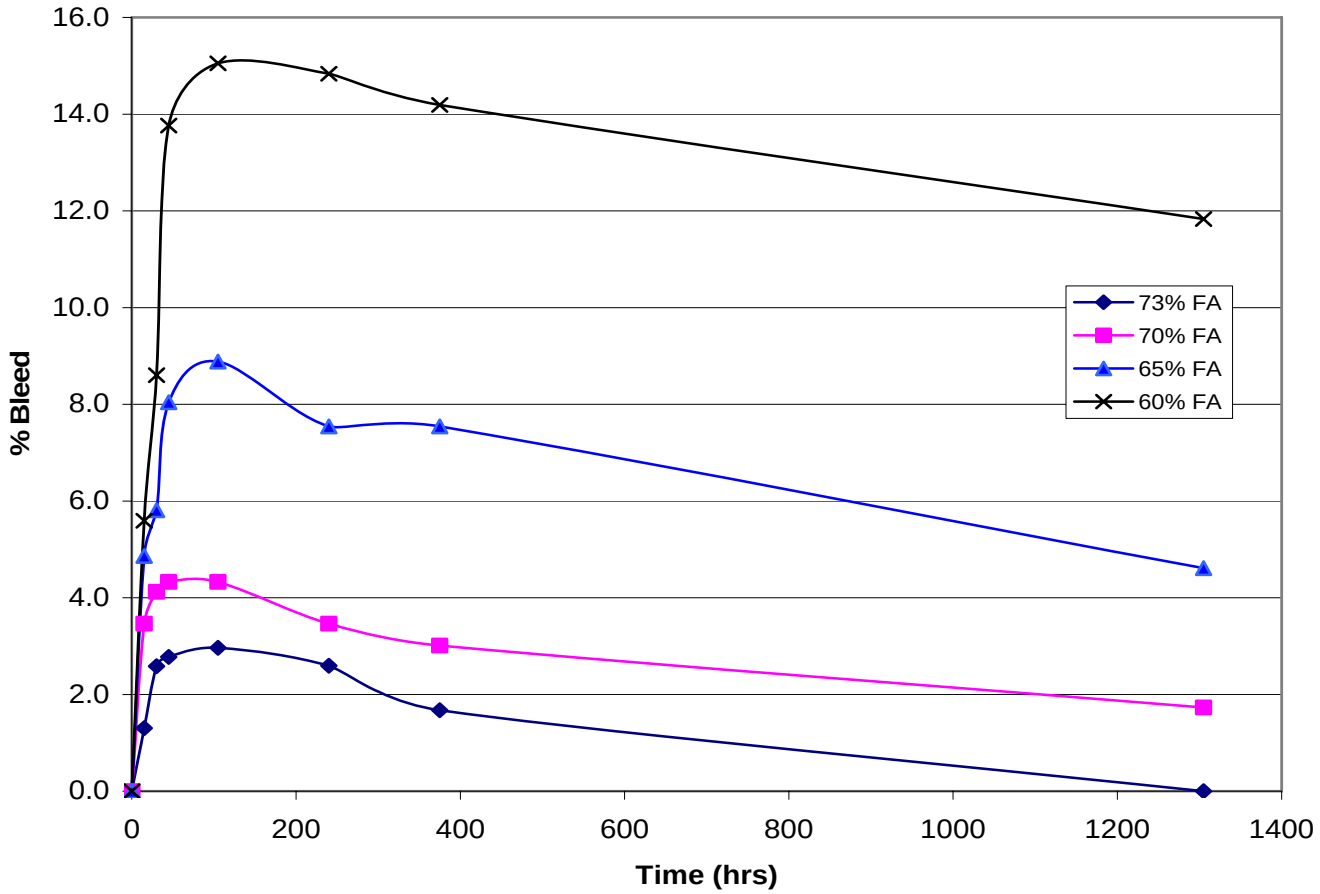

Fig. A2.1 Bleed behaviour of fly ash with distilled water

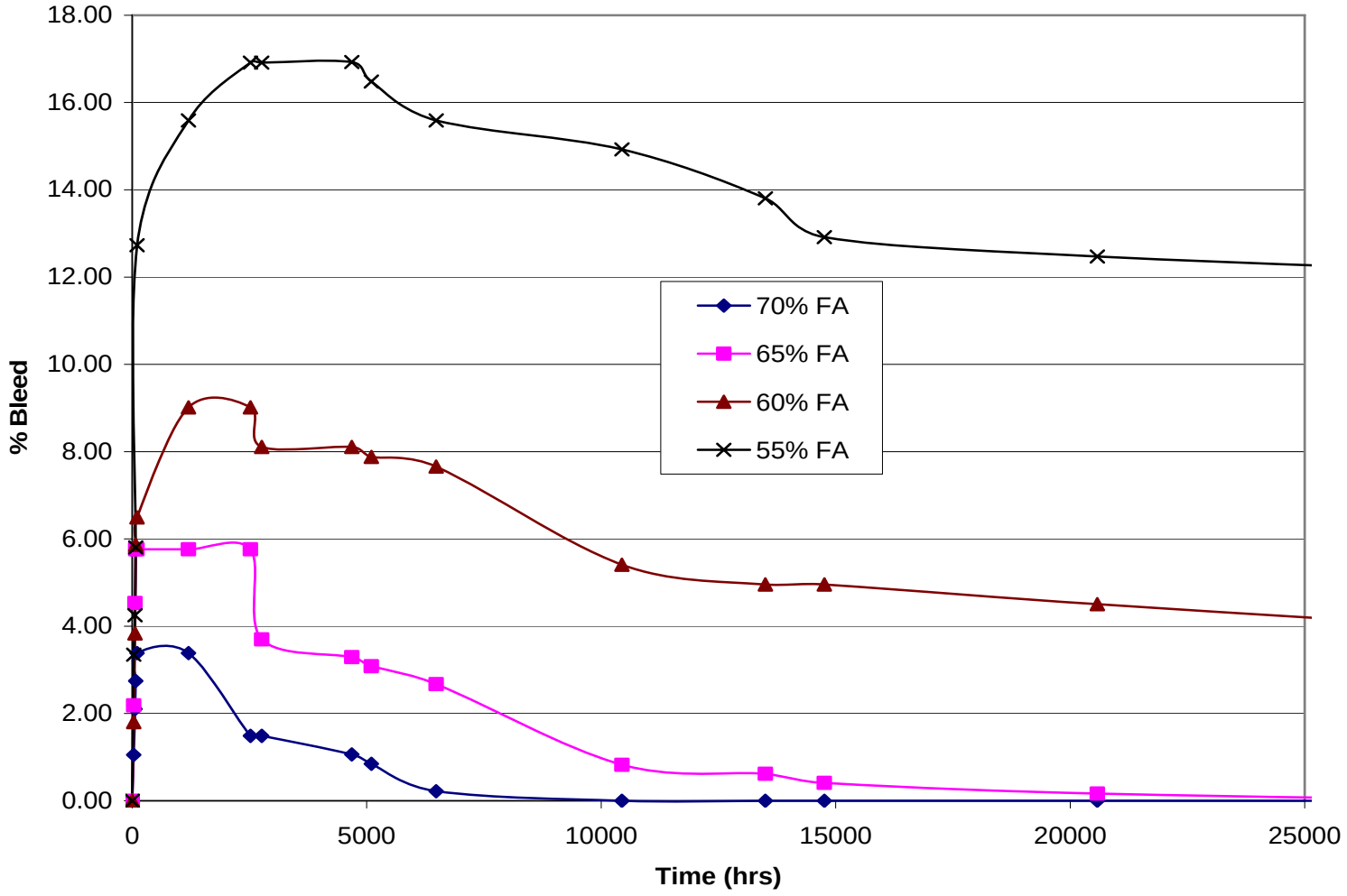

Fig. A2.2 Bleed behaviour of fly ash with U66 brine

A3: STATISTICS ON SLUMPING

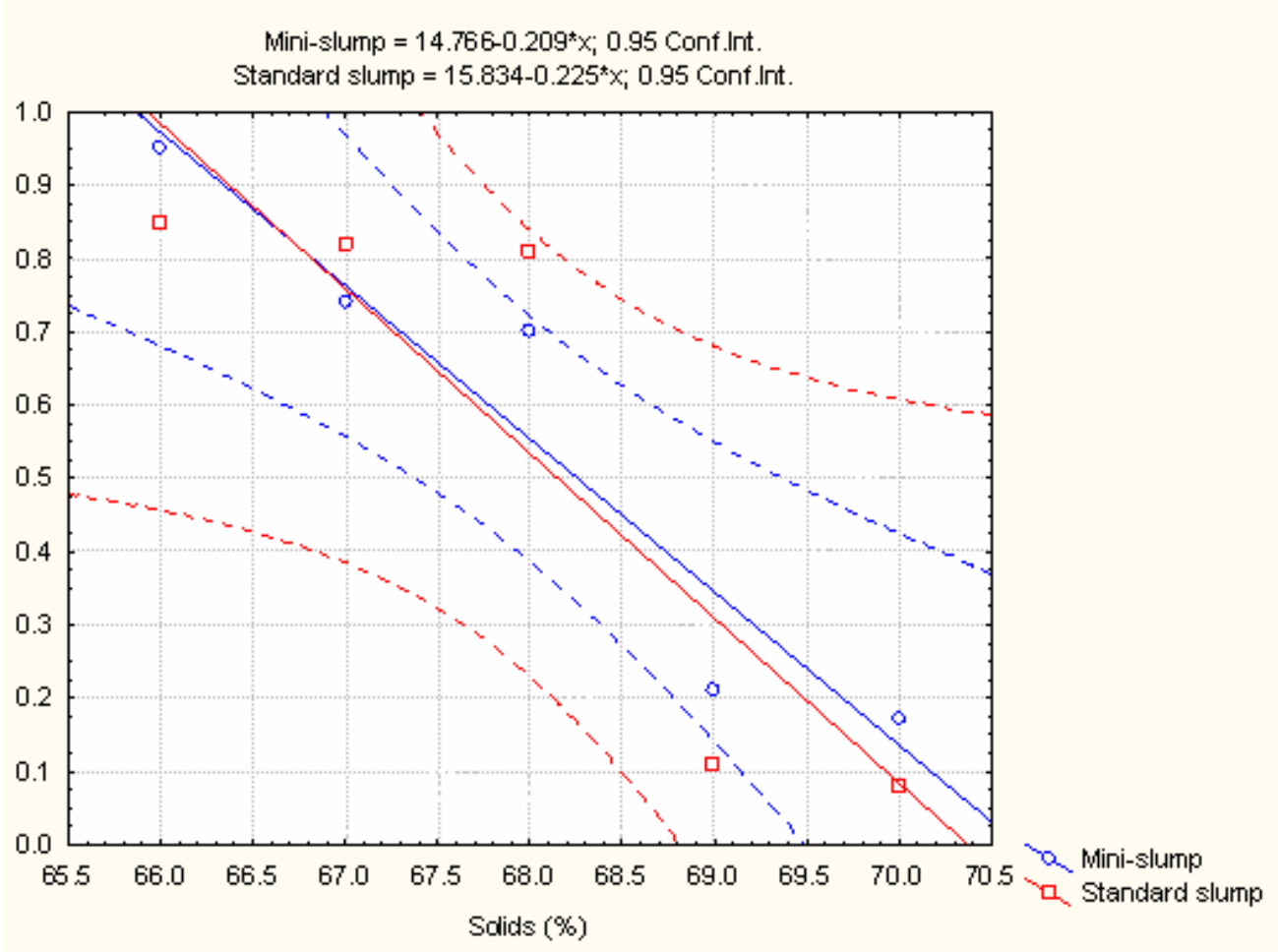

Fig. A3.1 Graph showing the relationship between two slump tests

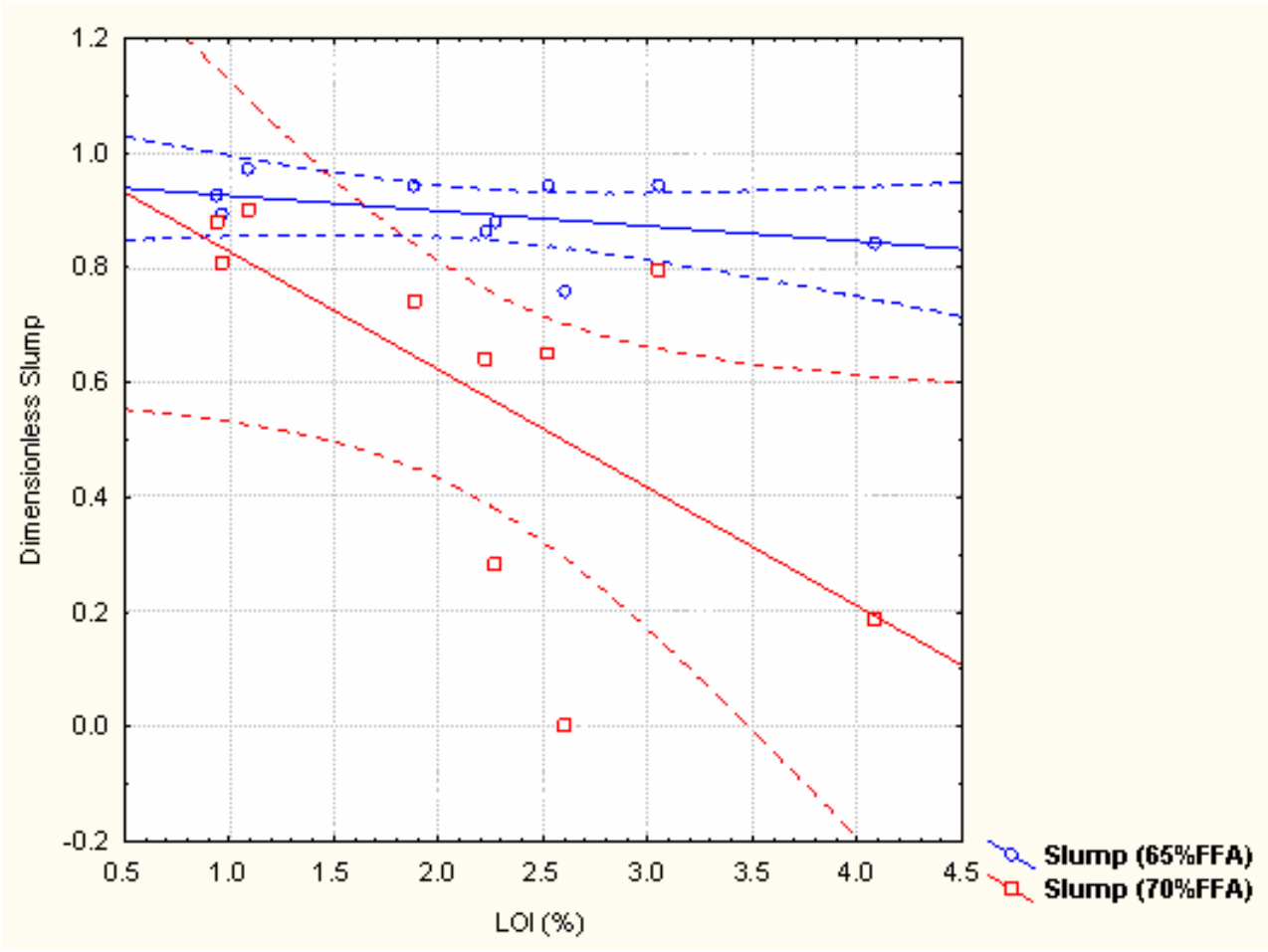

Fig. A3.2 The relationship between slump and LOI

APPENDIX B

ADDITIONAL DATA/RESULTS ON LEACHING

B1: CONDUCTIVITY GRAPHS ON EFFECT OF ADDITIVES

B1.1 Incineration Ash

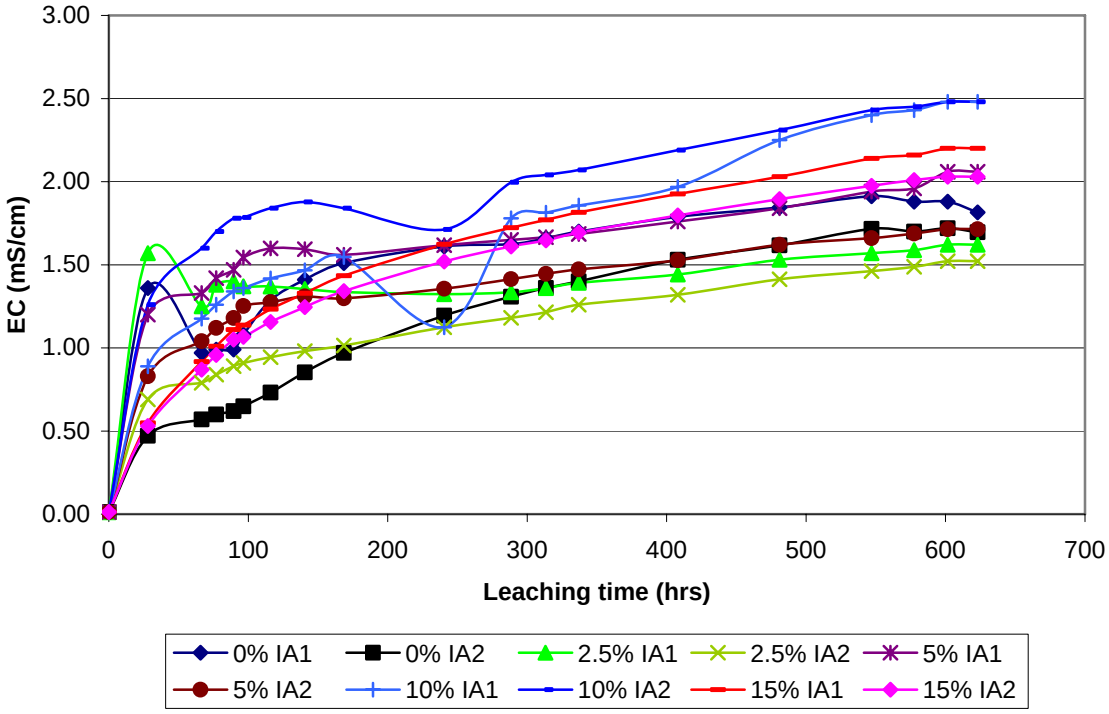

Fig. B1.1 Conductivity trend on pastes with IA

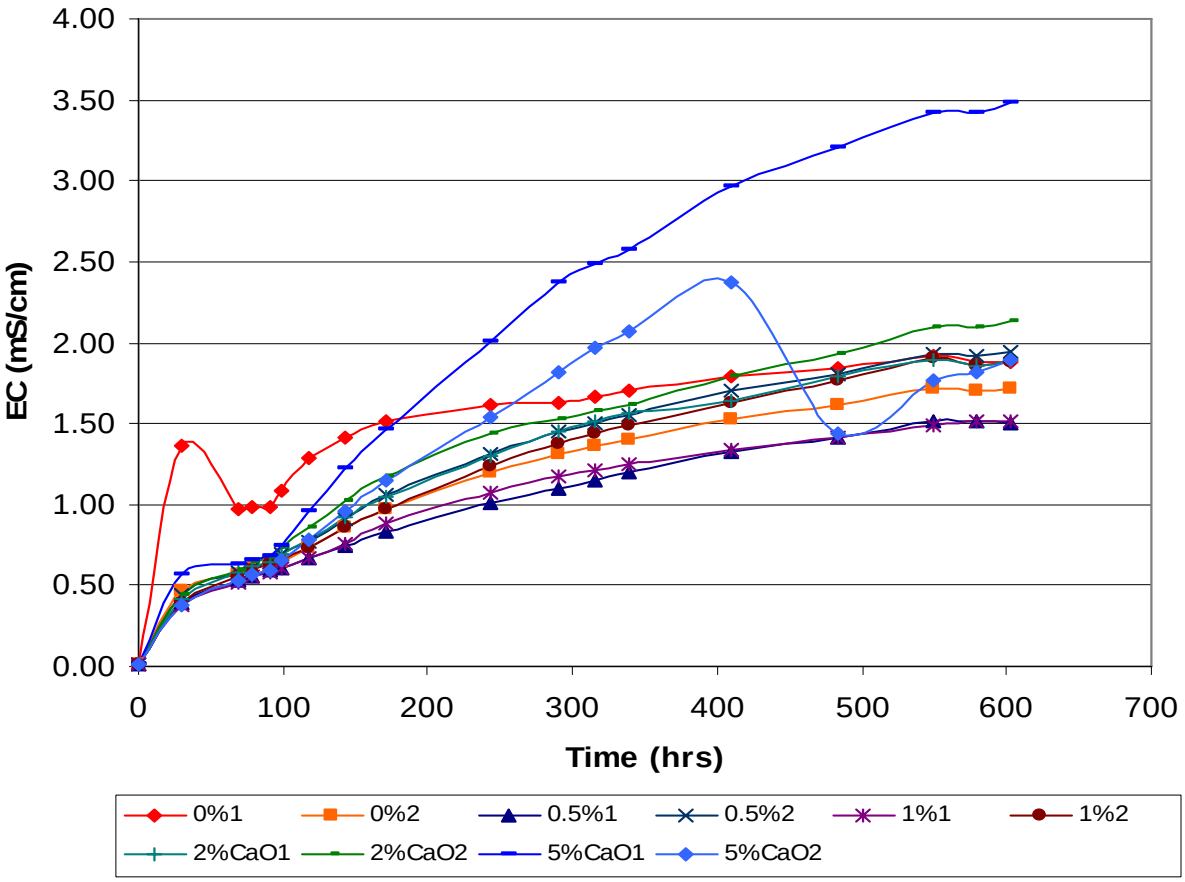

Fig. B1.2 Conductivity trend on pastes with lime

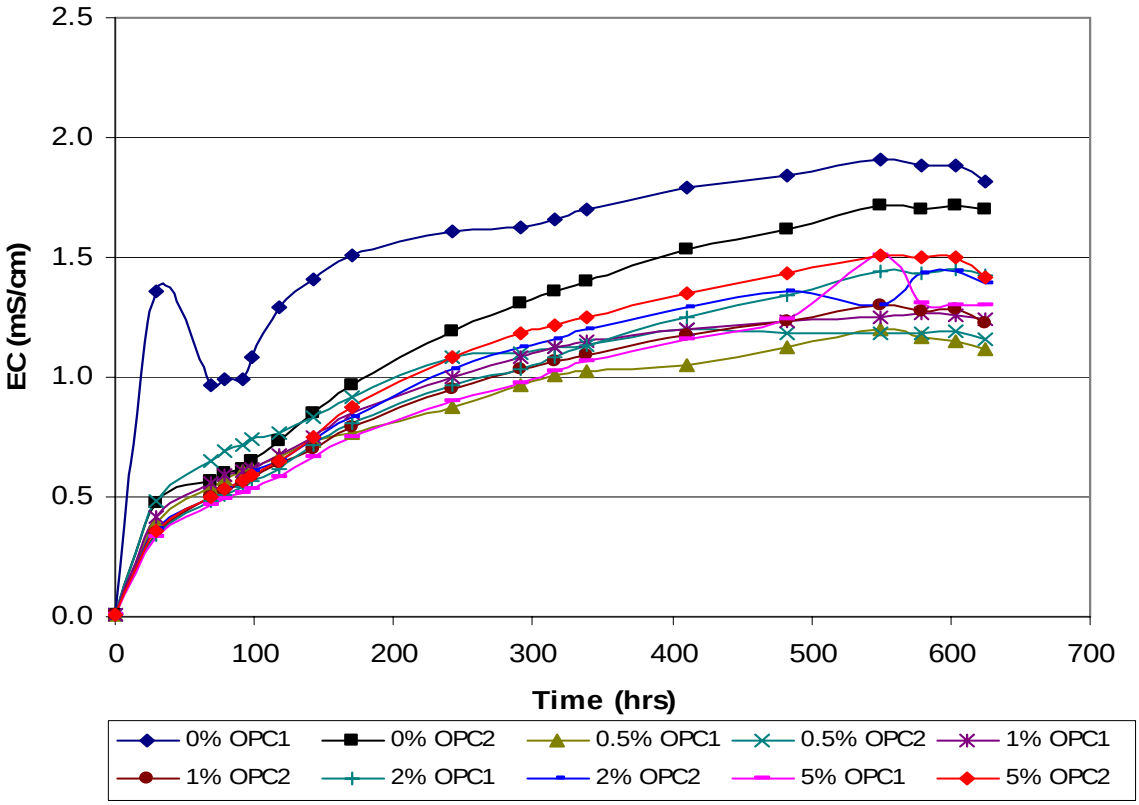

Fig. B1.3 Conductivity trend on pastes with cement

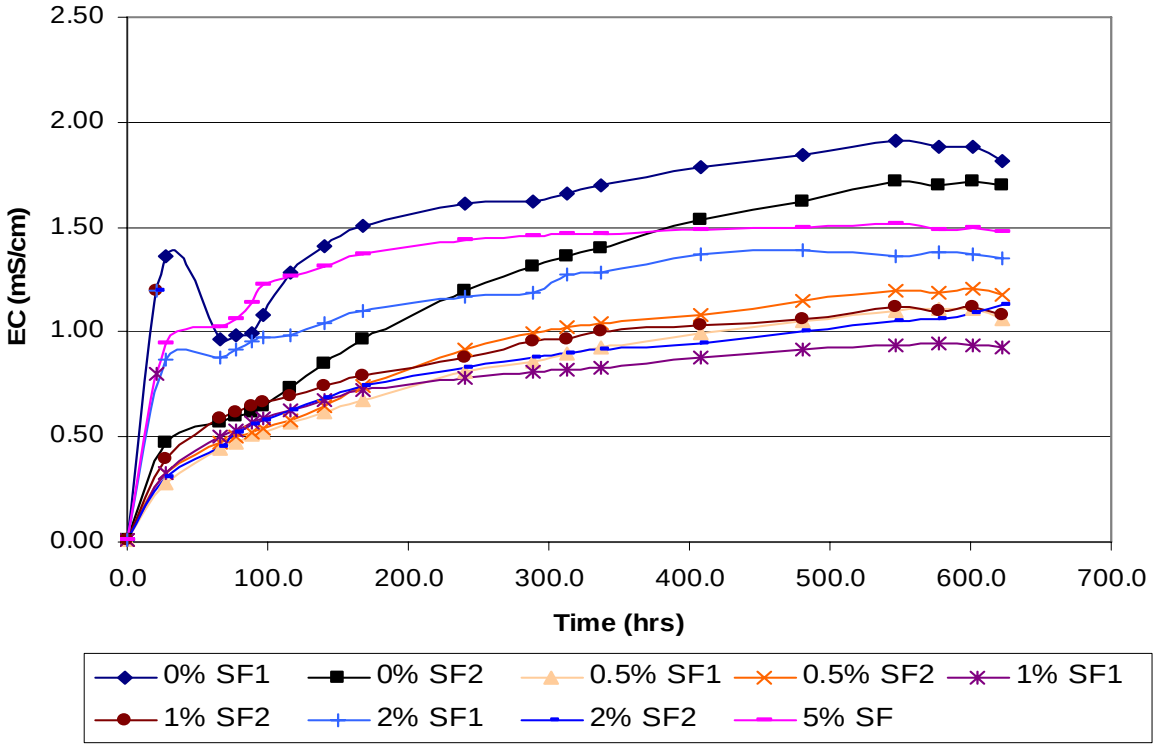

Fig. B1.4 Conductivity trend on pastes with silica fume

Table B1 Effect of SF in Permeability

% SF added to FA	Curing time (days)	permeability (cm/s)
0	9	4.0E-05
0	13	2.0E-05
2.5	12	2.4E-03
5	12	4.3E-03

B2: STATISTICAL DATA ASSESSING THE EFFECT OF SURFACE AREA IN LEACHING

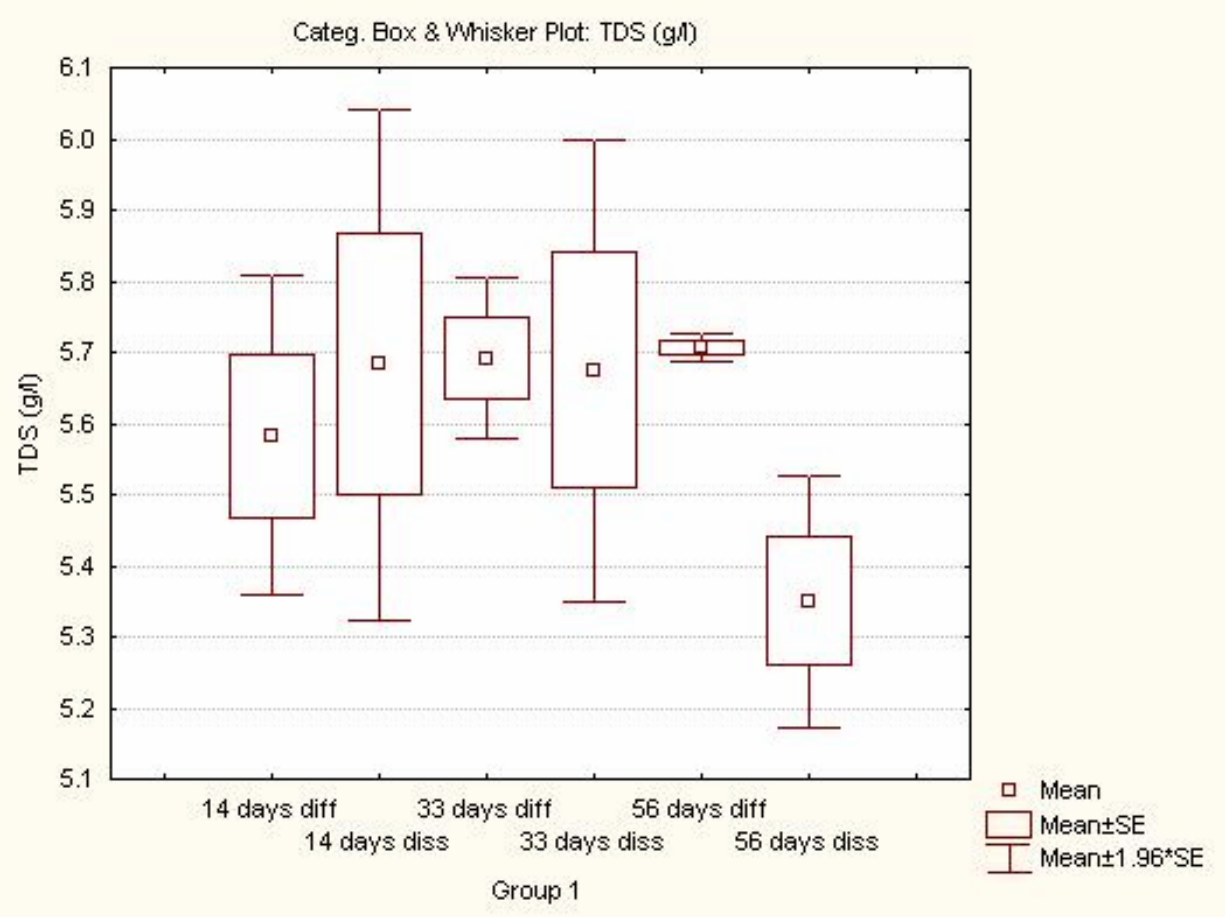

Fig. B2.1 Statistical results on TDS for curing and surface area

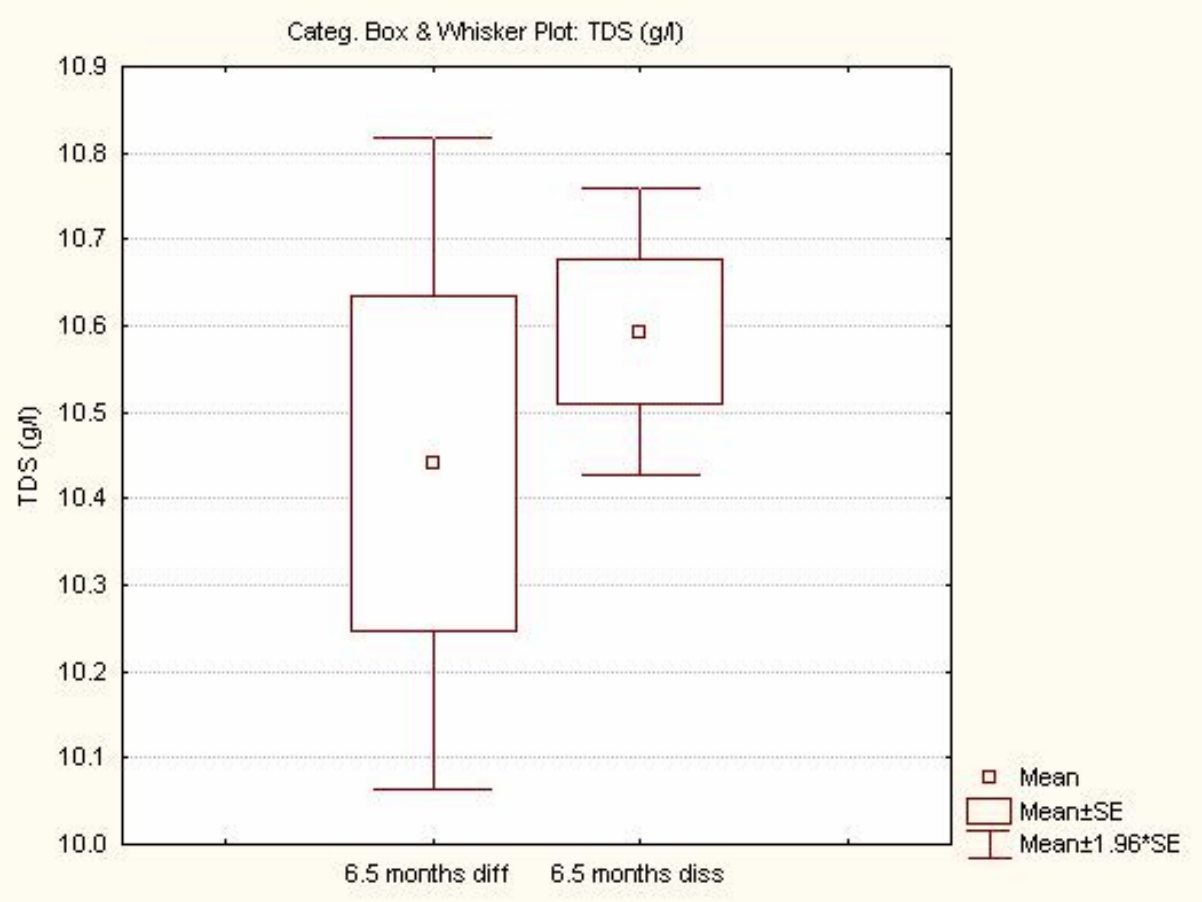

Fig. B2.2 Statistical results on leachate TDS for 6.5 month old paste (surface area)